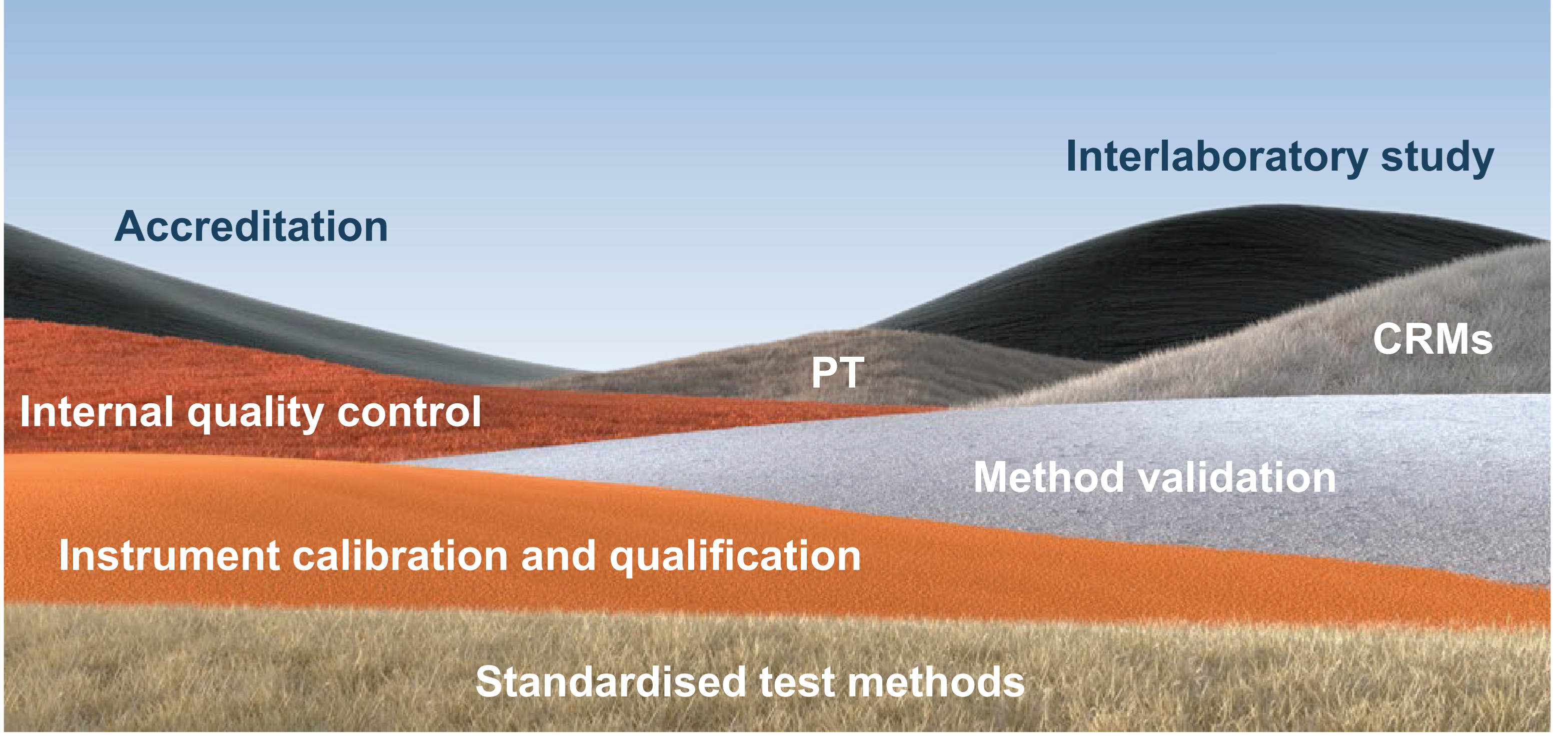
30 years of Measurement Uncertainty in Chemistry

A retrospective and a forward look

Steve Ellison, LGC Limited, Guildford, UK

Prehistory – before the GUM




1993 – Modern history begins


1993 – Modern history begins
Measurement Uncertainty

0 AG – A new challenge

Measurement Uncertainty

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The GUM - Measurement models and ‘propagation of uncertainty’

Mathematical form of uncertainty

$$y = f(x_1, x_2, \ldots, x_n)$$

$\boldsymbol{y}$ measurement result

$\boldsymbol{x_i}$ parameter affecting analytical result $\boldsymbol{y}$

Sometimes called a "**measurement model**" or "**measurement equation**"

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Mathematical form of uncertainty

$$y = f(x_1, x_2, \ldots, x_n)$$

$$u(y) = \sqrt{\sum_i^n \left(\frac{\partial y}{\partial x_i}\right)^2 u(x_i)^2}$$

↑ sensitivity coefficient

y measurement result

x_i parameter affecting analytical result $\boldsymbol{y}$

$u(x_i)$ uncertainty in $\boldsymbol{x_i}$

$u_i(y)$ uncertainty in $\boldsymbol{y}$ due to uncertainty in $\boldsymbol{x_i}$

$\partial y/\partial x_i$ Partial differential – a gradient

The "**law of propagation of uncertainty**"

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Uncertainty propagation

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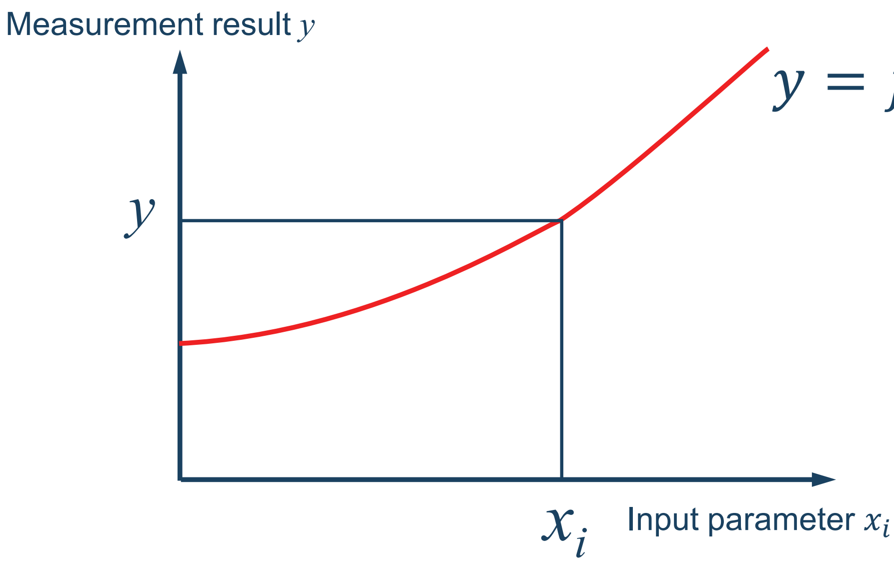

$$y = f(x_i, \dots)$$

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Uncertainty propagation

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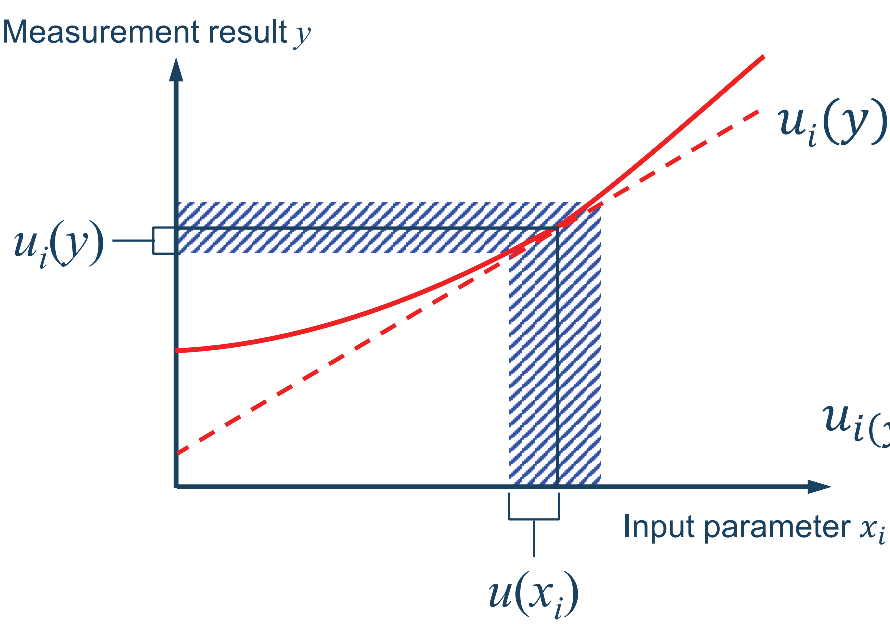

$$u_i(y) \approx \text{gradient} \times u(xi)$$

sensitivity coefficient

$$u_{i(y)} \approx \frac{\partial y}{\partial x} \times u(x_i)$$

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Other key features of the GUM

- Adoption of INC-1 1980 Recommendations
  - The uncertainty in the result of a measurement generally consists of several components which may be grouped into two categories according to the way in which their numerical value is estimated:

    A. those which are evaluated by statistical methods,

    B. those which are evaluated by other

No simple correspondence between categories A or B and ... "random" and "systematic"

Other key features of the GUM (cont)

- Adoption of INC-1 1980 Recommendations
  - Components in category A are characterized by estimated variances and degrees of freedom
  - The components in category B should be characterized by quantities u_j^2 **which may be considered as approximations to the corresponding variances**

Type A and Type B are treated in the same way

  - The combined uncertainty should be characterized by the numerical value obtained by applying the usual method for the combination of variances.

The first Eurachem guide

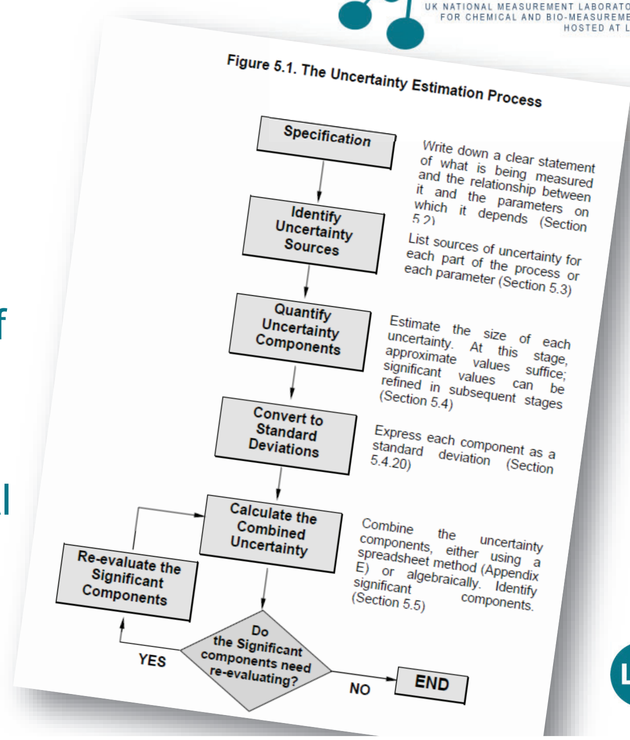
Eurachem

A focus for analytical chemistry in Europe

Quantifying Uncertainty in Analytical Measurement

Development of the first Eurachem guide

- Begun c. 1992-3 in the new MU working group of a young Eurachem
- Initial draft adopted the principles of the (then) draft ISO TAG 4 document
- Closely followed the 'law of propagation of uncertainty'
- Provided a process
- Provided worked examples from analytical chemistry
- Published in 1995
  – with intent to gather experience and review

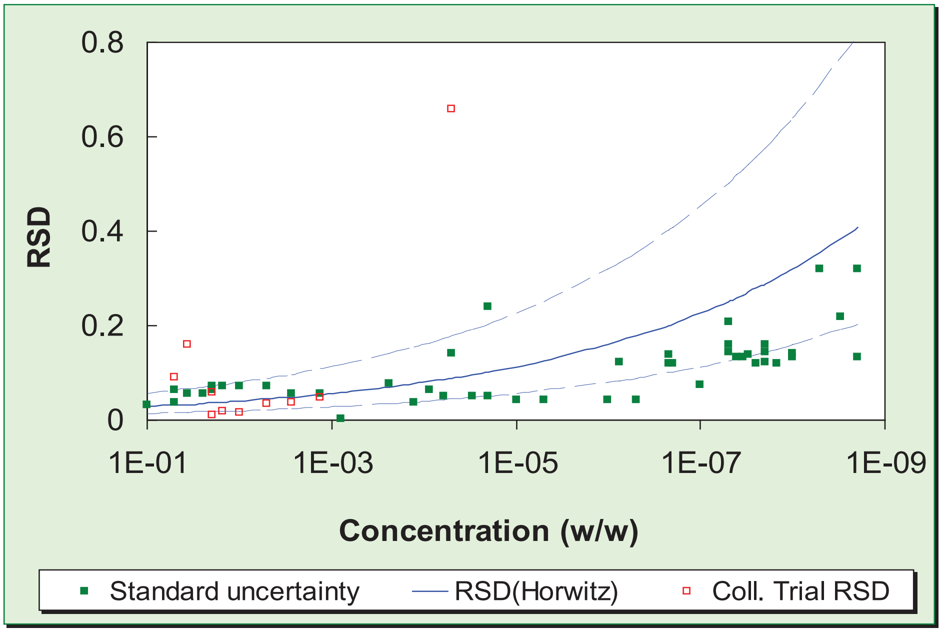


Emerging problems

Problems implementing the ISO Guide approach

- Difficult to write an equation that includes all influence factors
  - what about sample clean-up conditions, recovery of analyte from matrix, instrument conditions, interferences….
- Challenging to evaluate individual uncertainty components
- Process is too time consuming and unworkable in routine testing laboratories
  - a ‘reasonable estimation’ is required

Comparing u with s_R



Laboratory uncertainties using GUM tended to be smaller than reproducibility SD at lower concentrations

Additional problems

- Uncertainties dependent on level
  - No guidance on how to handle 'top down' uncertainties expressed as RSD
- Uncertainties near detection limits
  - Should results and uncertainties be reported below LOD?

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Developments in MU evaluation

1995-2000

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Cause-and-effect analysis

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Accred Qual Assur (1998) 3:101–105

GENERAL PAPER

S. L. R. Ellison
V. J. Barwick

Estimating measurement uncertainty: reconciliation using a cause and effect approach

Received: 28 October 1997
Accepted: 17 November 1997

Presented at: 2nd EURACHEM Workshop on Measurement Uncertainty in Chemical Analysis, Berlin, 29–30 September 1997

Abstract A strategy is presented for applying existing data and planning necessary additional experiments for uncertainty estimation. The strategy has two stages: identifying and structuring the input effects, followed by an explicit reconciliation stage to assess the degree to which information available meets the requirement and thus identify factors requiring further

promotes consistent identification of important effects, and permits effective application of prior data with minimal risk of duplication or omission. The results of applying the methodology are discussed, with particular reference to the use of planned recovery and precision studies.

Accreditation and Quality Assurance
1998

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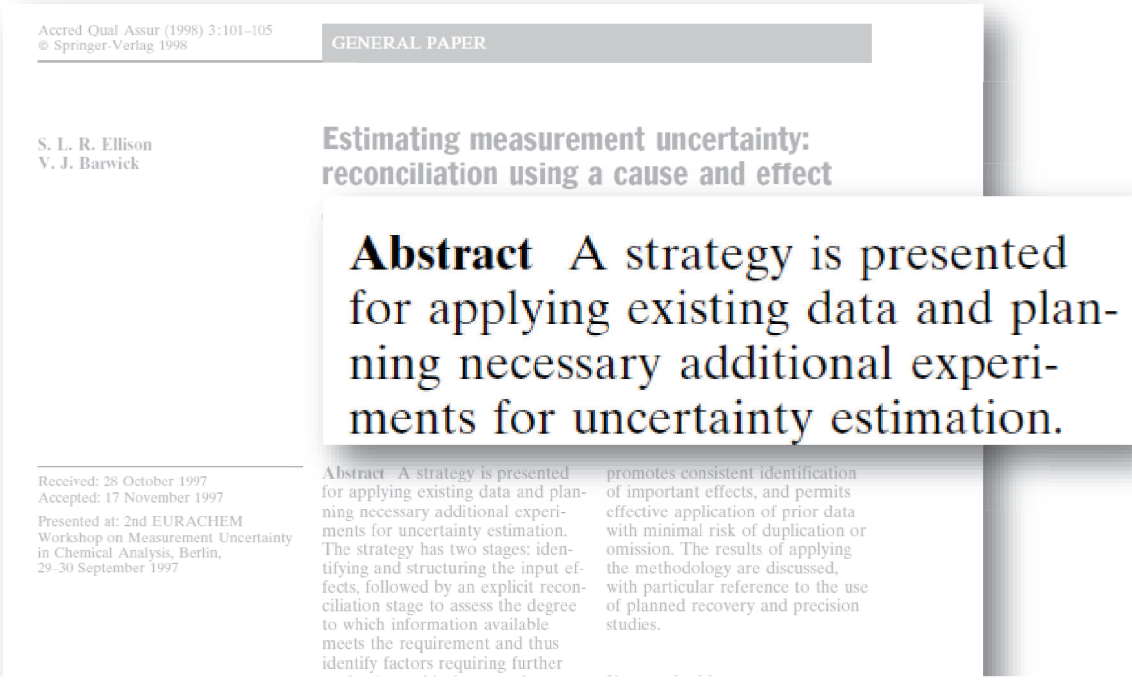
Cause-and-effect analysis



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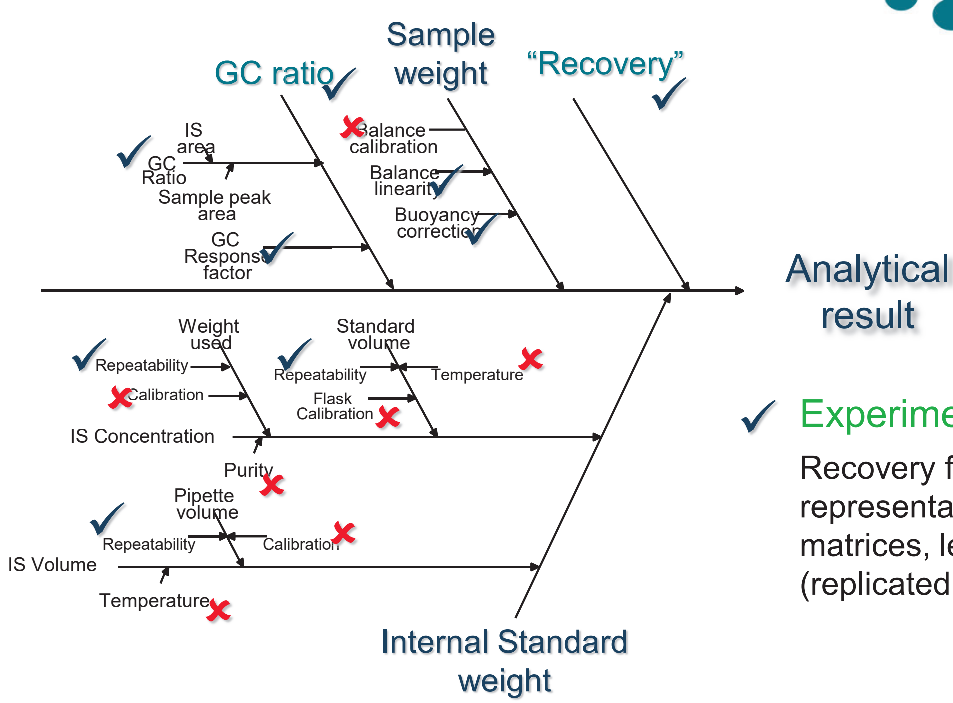
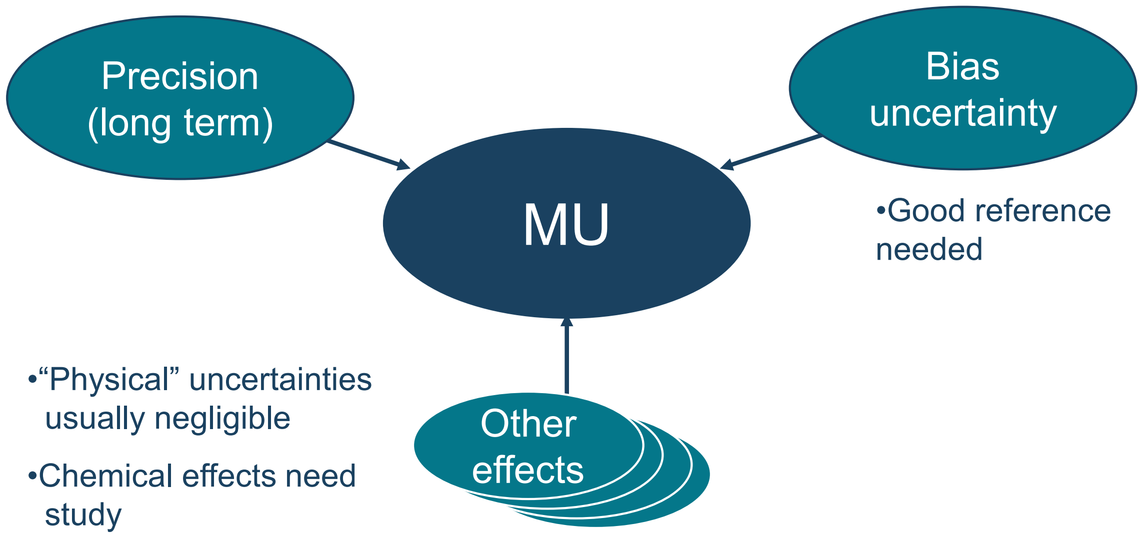
Cause-and-effect analysis
"Reconciliation" – what have we covered?



✓ Experiment:

Recovery for representative matrices, levels (replicated)

Top-down evaluation with additional effects



- Good reference needed

- "Physical" uncertainties usually negligible
- Chemical effects need study

A simple spreadsheet method

Analyst, October 1994, Vol. 119 2161

Tutorial Review

Calculating Standard Deviations and Confidence Intervals with a Universally Applicable Spreadsheet Technique

J. Kragten

Laboratory of Analytical Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

A quick and universally applicable spreadsheet method is outlined for the calculation of standard deviations based on the general formula for error propagation:

$$s_R^2 = \left(\frac{\partial R}{\partial x}\right)^2 s_x^2 + \left(\frac{\partial R}{\partial y}\right)^2 s_y^2 + \left(\frac{\partial R}{\partial z}\right)^2 s_z^2 + \ldots$$

With this method, standard deviations are calculated numerically without violating the condition of mutual independence, with a substantial time gain and with no risk of calculating errors. Satterthwaite's approximation of the degrees of freedom is a logical extension of the technique with which confidence intervals can be easily established. Direct insight is obtained about the separate contributions of the different error sources.

of x, y, . . ., the simple rules lead to erroneous results. This will be shown with the calculation of the surface of a block: $R = 2(lb + bh + hl)$. Most workers will split R into the parts lb, bh and hl. The rules are applied to these separate parts and the standard deviations of these separate parts are obtained. Eventually the separate parts are summed to obtain R and the simple error propagation rules are applied again to find s_R. At this point the error is made: commonly the separate parts of R have some variables in common and hence are mutually dependent. (Use of the word *correlation* is restricted to covariance between measured quantities. Terms containing the same variable in a mathematical relationship will be called *dependent*.) The block-surface $R = 2(lb + bh + hl)$ is a good example with the product terms lb, bh and hl sharing b, h and

Kragten, *Analyst* **1994**

Kragten's method
Spreadsheet implementation

	x	u							
m	100	2		102	100	100	100	100	
V_T	100	0.1		100	100.1	100	100	100	
α	0.001			0.001	0.001	0.001	0.001	0.001	
T	25	1.15		25	25	25	26.15	25	$x+u(x)$
T_0	25			25	25	25	25	25	
C	1	0.020		1.02	0.999001	1	1.00115	1	Recalculation
				0.02	-0.001	0	0.00115	0	Differences
				0.0004	9.98E-07	0	1.32E-06	0	$Diff^2$

Combined uncertainty

Details in QUAM

Quam:2000

Quantifying Uncertainty in Analytical Measurement

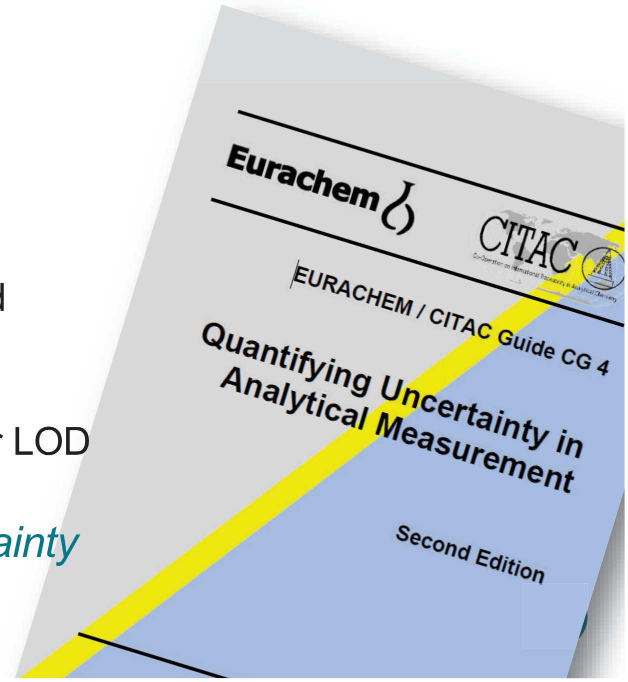
Second Edition

QUAM Second edition

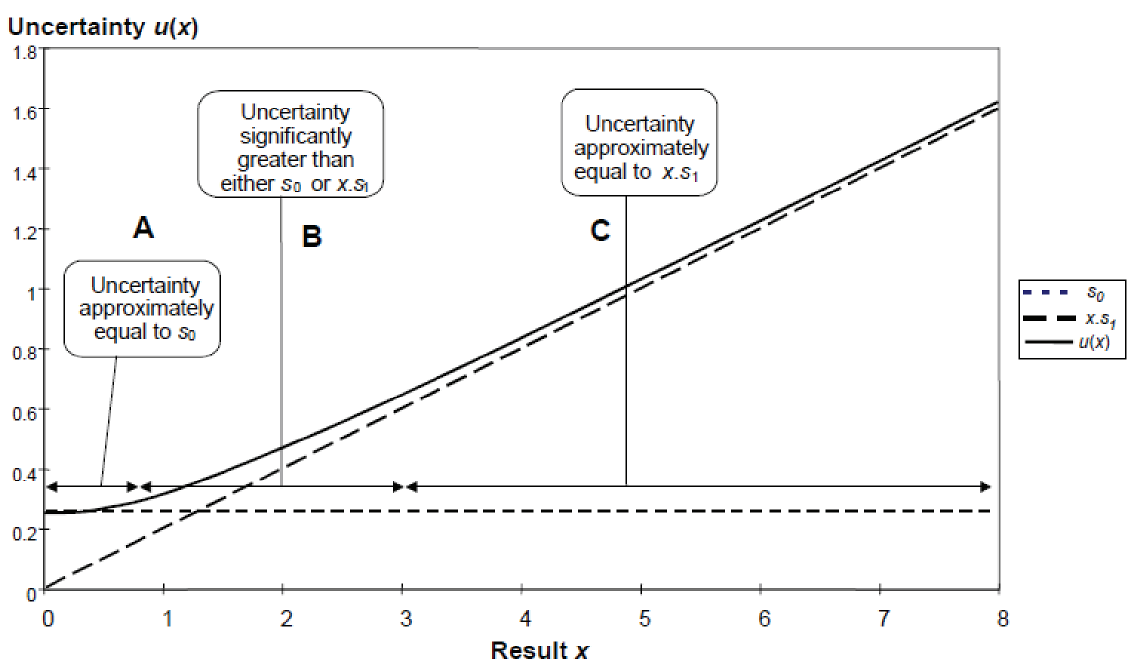
- Based on QUAM:1995
- Included
  - Clear guidance permitting use of validation data
  - Guidance on cause-and-effect analysis
  - Guidance on Kragten's method
  - All examples used cause-and-effect analysis and Kragten calculation

  - Basic guidance on results and uncertainties near LOD

    "The ideal is accordingly to report valid observations and their associated uncertainty regardless of the values."



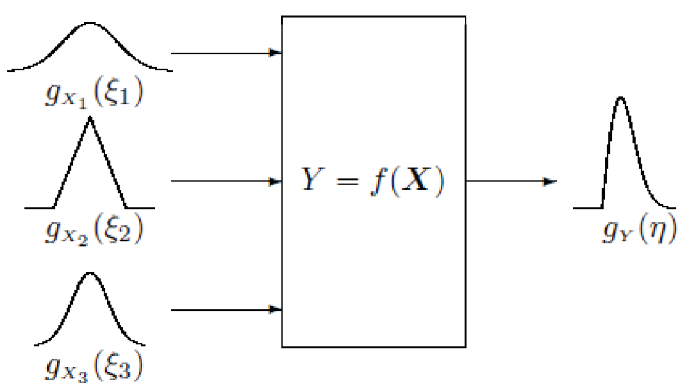
Dealing with uncertainties dependent on level



2000 –2012: Further developments

GUM Supplement 1 (JCGM 101)

– *Evaluation of measurement data — Supplement 1 to the "Guide to the expression of uncertainty in measurement" — Propagation of distributions using a* ***Monte Carlo method***



Illustrations from JCGM:101, Figures 2 & 3

New approaches to uncertainty near LOD

www.rsc.org/analyst | The Analyst

PAPER

Reporting measurement uncertainty and coverage intervals near natural limits

Simon Cowen and Stephen L. R. Ellison

Received 21st December 2005, Accepted 24th April 2006
First published as an Advance Article on the web 11th May 2006
DOI: 10.1039/b518084h

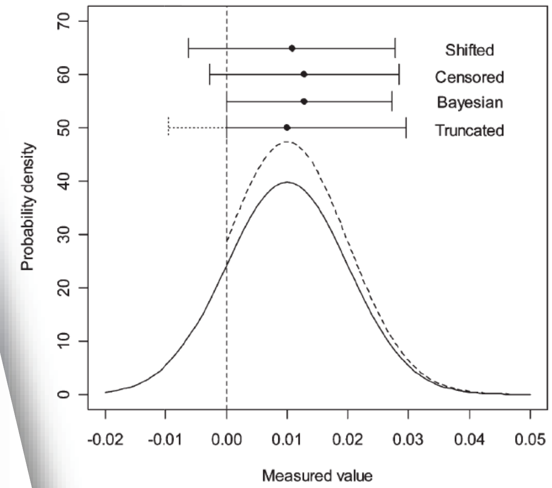
Different methods of treating data which lie close to a natural limit in a feasible range, such as zero or 100% mass or mole fraction, are discussed and recommendations made concerning the most appropriate. The methods considered include discarding observations beyond the limit, shifting observations to the limit, truncation of a classical confidence interval based on Student's *t* (coupled with shifting the result to the limit if outside the feasible range), truncation and renormalisation of an assumed normal distribution, and the maximum density interval of a Bayesian estimate based on a normal measurement distribution and a uniform prior within the feasible range. Based on consideration of bias and simulation to assess coverage, it is recommended that for most purposes, a confidence interval near a natural limit should be constructed by first calculating the usual confidence interval based on Student's *t*, then truncating the out-of-range portion to leave an asymmetric interval and adjusting the reported value to within the resulting interval if required. It is suggested that the original standard uncertainty is retained for uncertainty propagation purposes.

Introduction

Analytical measurement is concerned with the quantitation of some or all of the constituents of a sample, together with a ... assessment of the uncertainty associated with the result. ... principles of measurement uncertainty ... *Guide to the Expression of* ... and elaborated ...

• Establishment of the detection limit for an instrument and method.

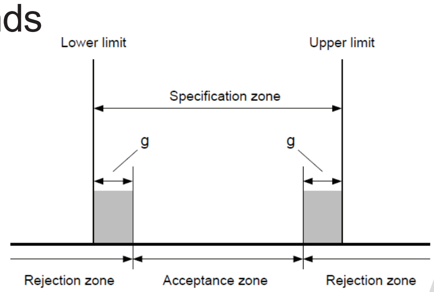
Assuming that systematic errors are absent or have been accounted for in the instrument or method being used, the remaining uncertainty arises from effects which can be assumed to have random contributions to the observed result.[1] For example, the variability in a set of replicates is the random error due to instrument (or method) repeatability, and the actual deviation from the value of the measurand has (within ... uncertainty) unknown sign and magnitude. ... arises from effects other than sample ... are not constrained ...



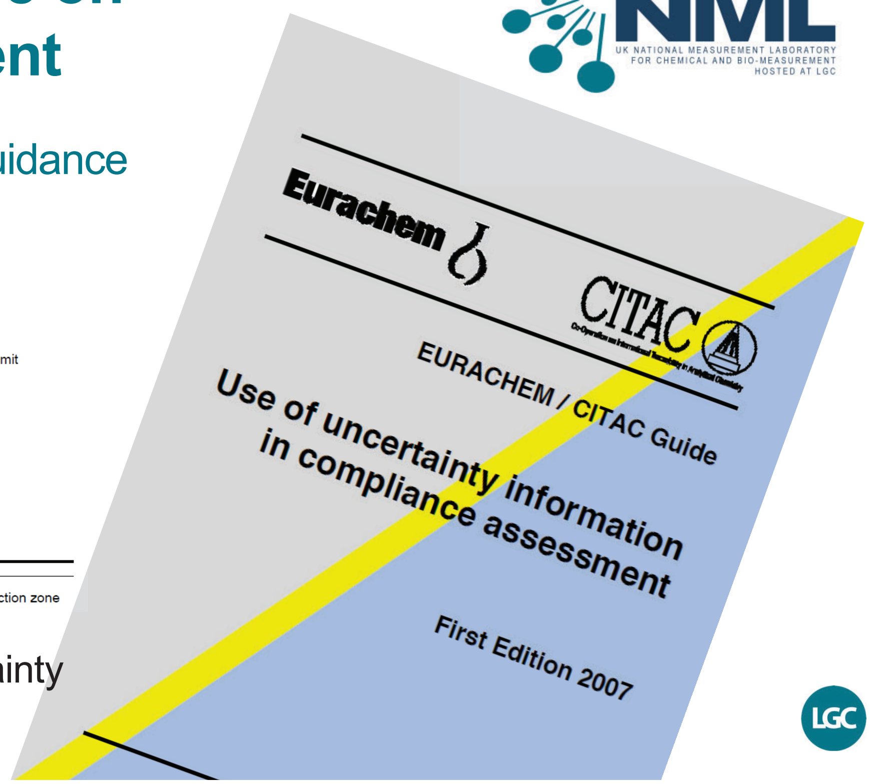
DOI: 10.1039/b518084h

New detailed guidance on conformity assessment

- Published as supplementary guidance
- Introduced 'new' ideas
  - Decision rules
  - Guard bands



  - Decisions under relative uncertainty



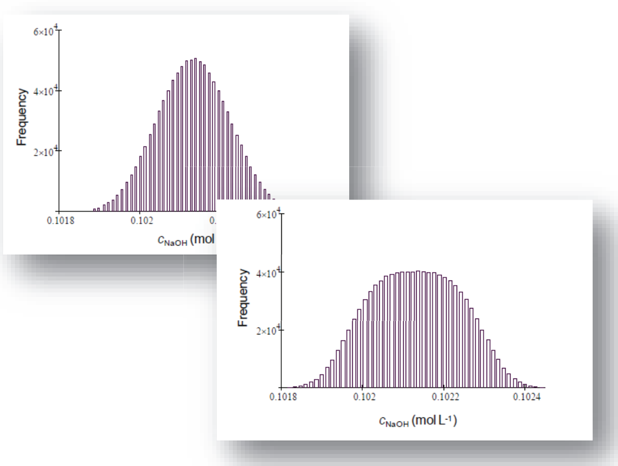
Quam:2012

Quantifying Uncertainty in Analytical Measurement

Third Edition

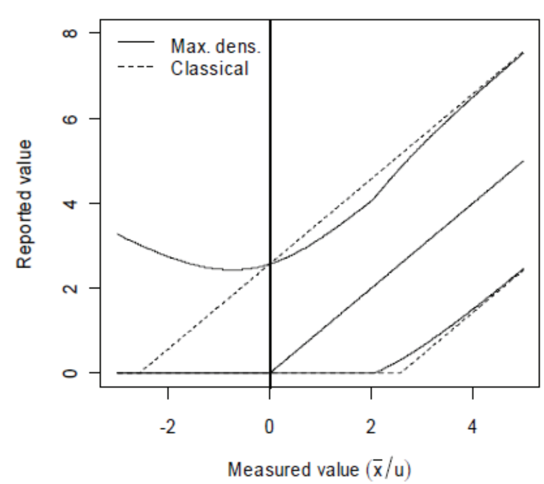
Additional material

Monte Carlo examples



Uncertainties near zero

- Bayesian solution



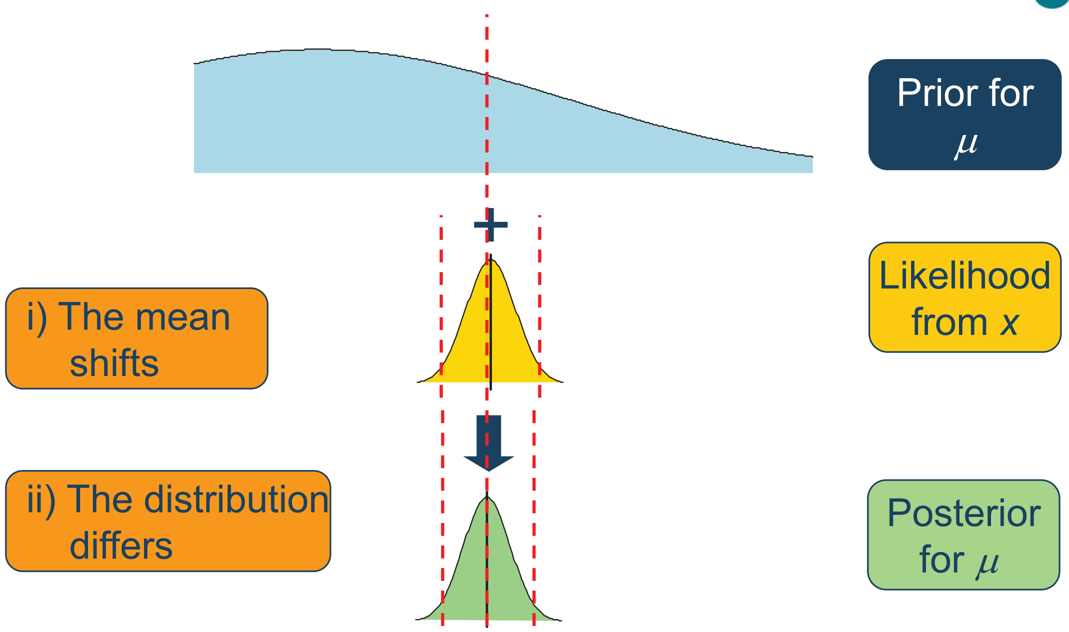
2013 – 2025: Evolution continues

The Uncertainty Factor

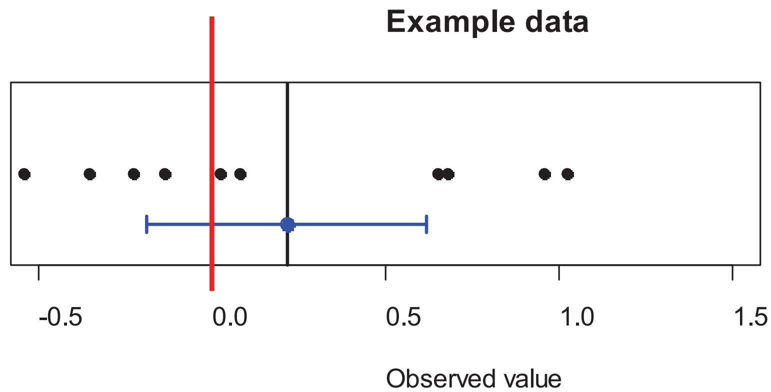
- Introduced in the Eurachem guide on Uncertainty from Sampling (2nd Edition)
- Gives an asymmetric interval
- Useful for large relative uncertainty with approximately lognormally distributed uncertainty

Accred Qual Assur (2015) 20:153–155
DOI 10.1007/s00769-015-1115-6

Bayes applied to Measurement Uncertainty

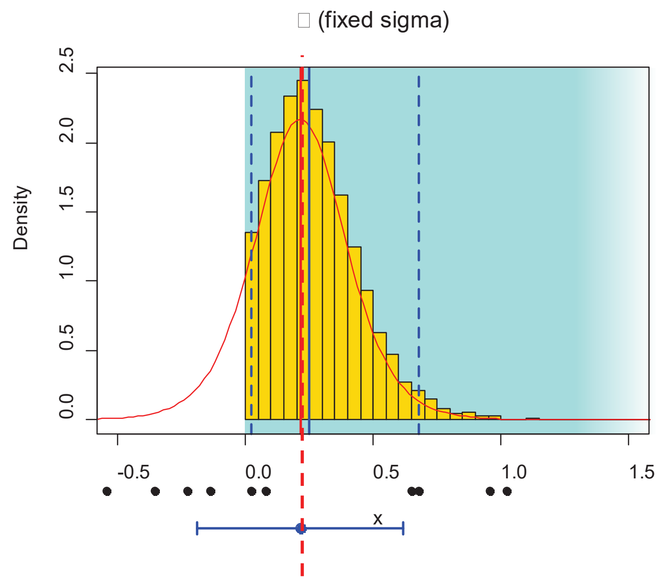


MCMC example 2: Constant RSD - SD proportional to μ

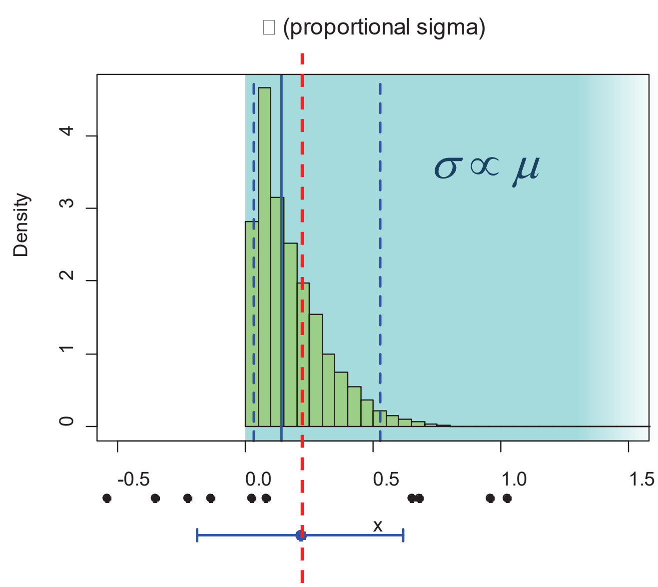


- Concentration: not below zero
- Common observation: standard deviation proportional to true value

MCMC results:
i) Fixed standard deviation



MCMC results
ii) Proportional standard deviation



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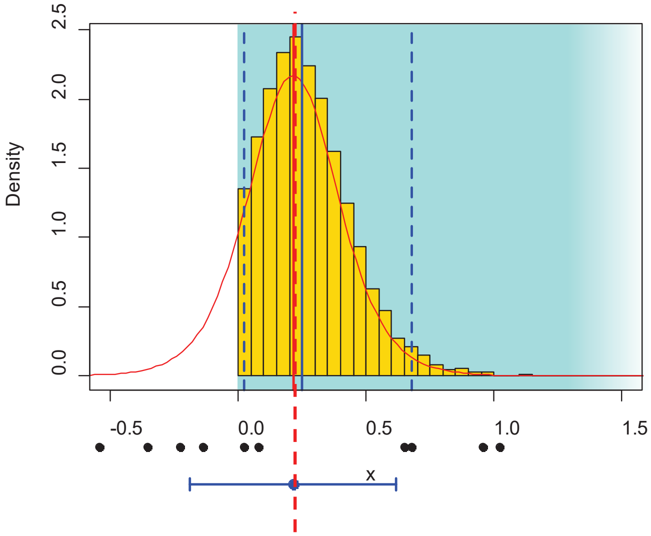
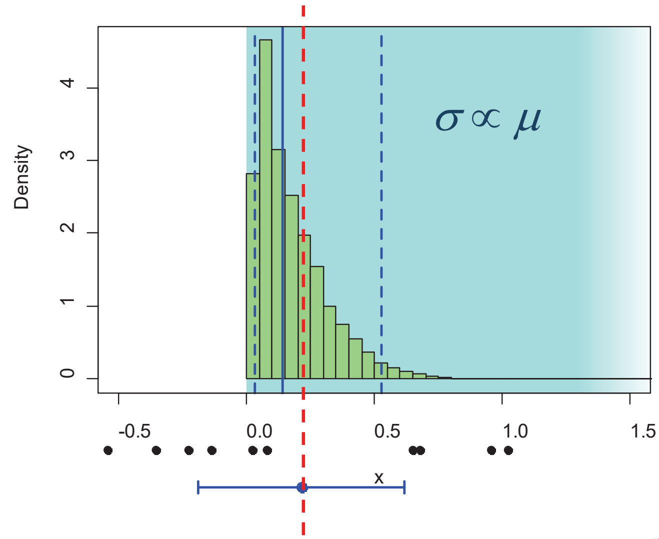
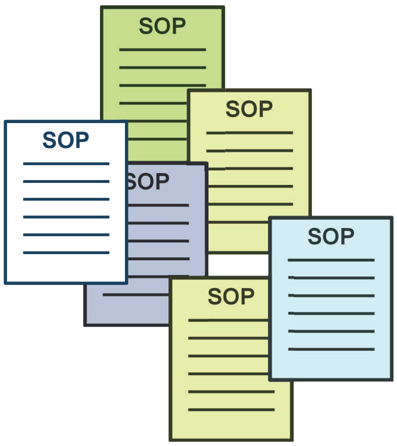


ii) Proportional standard deviation



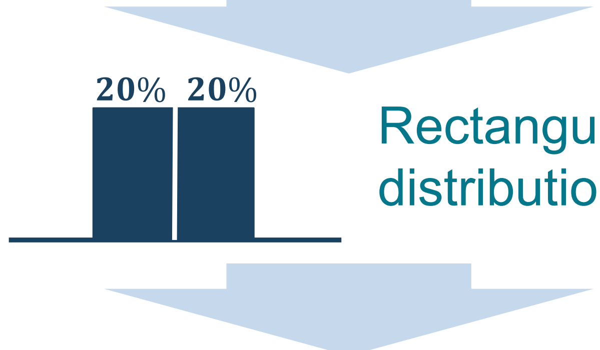
Outstanding problems

Allowable limits and measurement uncertainty – A problem?



Permitted Recovery

$$100 \pm 20\ \%$$



Rectangular distribution

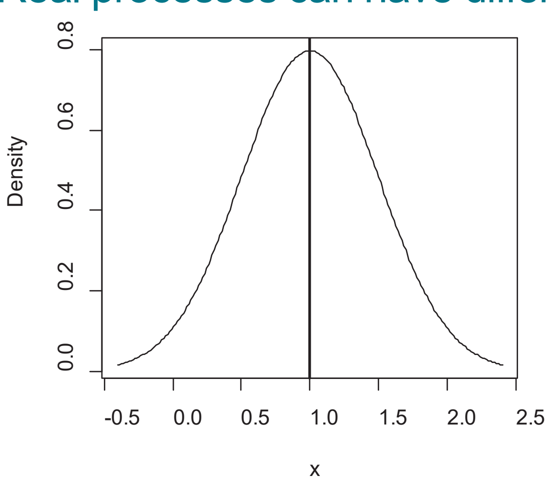
Recovery

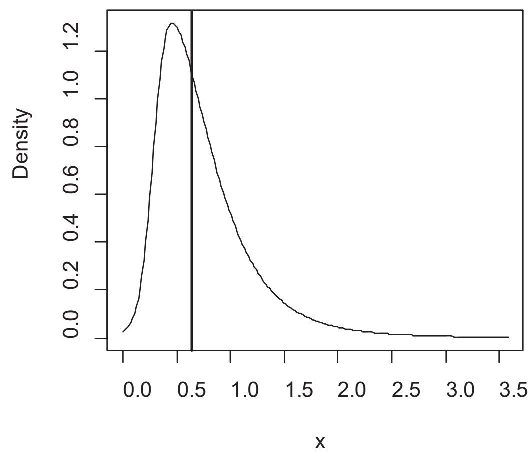
$$100 \pm 20\%$$

$$u = \frac{20}{\sqrt{3}} = 11.5\ \%$$

Asymmetry – What does it mean for conformity assessment?

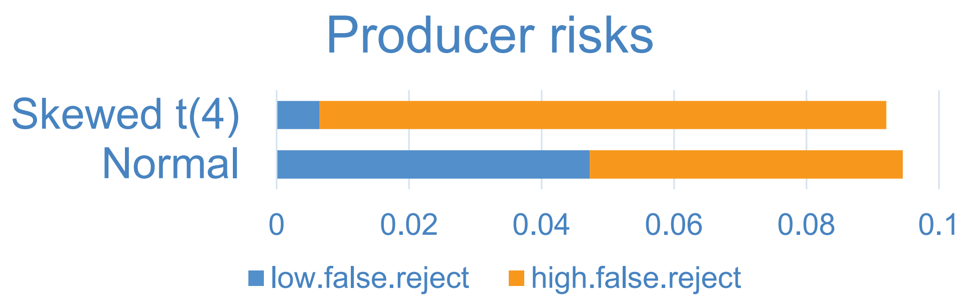
- Real processes can have different distributions

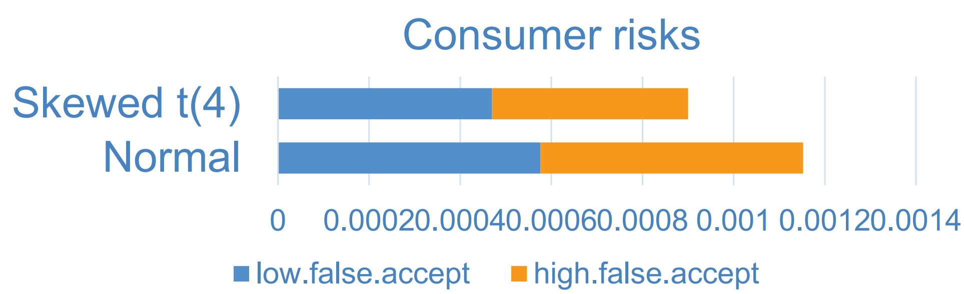




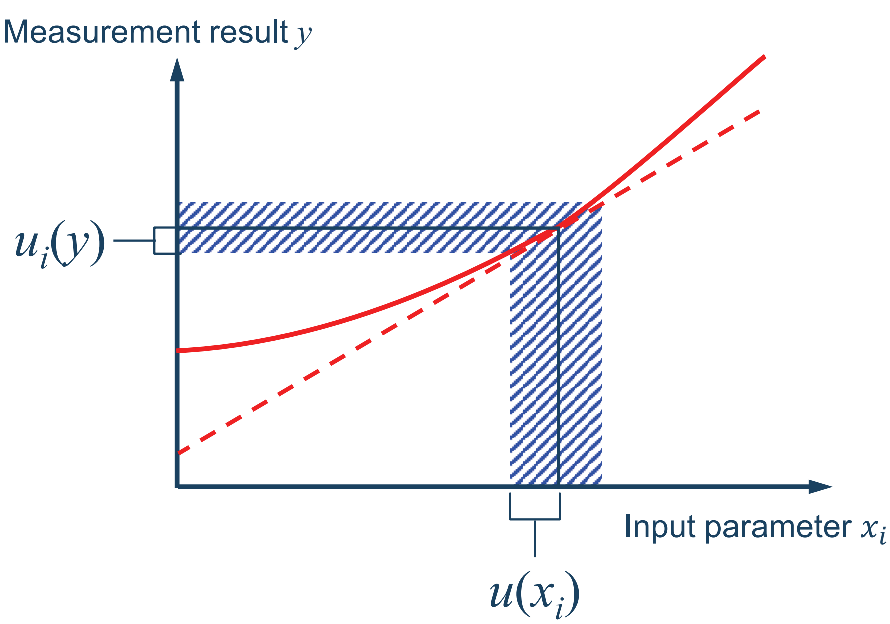
- Does this affect conformity assessment using MU?

Asymmetry – What does it mean for conformity assessment?





Linearity – How linear is ‘linear enough’?



The Future

Future MU guidance from Eurachem

- New guidance on MU from validation data
  - Current guide gives general guidance
  - Additional ‘how to’ guidance needed
  - Draft guide now out for consultation

- Additional guidance in QUAM
  - Uncertainty factors
  - Asymmetry – cautionary guidance
  - Non-linearity – cautionary guidance
  - Bayesian methods ??
  - Effect of permitted limits on MU – Supplementary guidance ?


Conclusion
Measurement Uncertainty


Conclusion
Measurement Uncertainty
- Not the mountain it once was
- ... But work still to do