



The new Eurachem/CITAC Guide: a summary of structure and changes

S L R Ellison
LGC Limited, Teddington, UK

Uncertainty evolution



Pre-1978 Random/systematic error; Error propagation in chemistry (Eckshlager 1961); Collaborative study

- | | |
|---|--|
| <p>1980 • BIPM INC-1 (1980)
– Type A / Type B</p> <p>1982 – Combine as variances</p> <p>1986</p> <p>1993 • ISO Guide</p> <p>1995 • EURACHEM Guide 1st ed</p> <p>2000 • EURACHEM Guide 2nd ed (QUAM:2000)</p> <p>2010 • GUM Supplement 1 (MCS)</p> | <p>• AOAC Stats manual (<i>Development/validation</i>)</p> <p>• ISO 5725:1986 (<i>Collab trial</i>)</p> <p>• ISO 5725:1994 (<i>Adds trueness</i>)</p> <p>• <i>ISO 21748 – Uncertainty from collab study data</i></p> |
|---|--|



• **3rd Edition EURACHEM/CITAC guide**

Principles of the Revision



- Remember translators
 - Do not revise 'cosmetically' – keep existing text wherever possible
- Refer to existing guidance where possible
 - Do not re-state other guides
- Add new sections rather than intersperse modifications
- Adopt any known corrections

A note on Terminology



- VIM 3 is published
 - Why not update to VIM 3 terminology throughout?
- QUAM:2012 Implements the GUM
 - needs to use GUM terms
- It is for Chemists
- VIM 3 definitions are often quite different in wording and need explanation
- There's a detailed Eurachem guide to VIM 3
- Decision:
 - Use GUM terminology with discussion of VIM terms where different

QUAM:2012 - Contents



- Foreword to the third edition
- 1. Scope and field of application
- 2. Uncertainty
- 3. Analytical measurement and uncertainty
- 4. The process of measurement uncertainty estimation
- 5. – 8. Detailed guidance on steps in measurement uncertainty estimation
- 9. Reporting uncertainty

Appendices



- A. Examples
- B. Definitions
- C. Uncertainties in analytical processes
- D. Analysing uncertainty sources
- E. Useful statistical procedures
- F. Measurement uncertainty at the limit of detection/limit of determination
- G. Common sources and values of uncertainty
- H. Bibliography

Scope



- Evaluation of ... uncertainty ... for a single method implemented as a defined measurement procedure in a single laboratory.
- [Use of] Information from method development and validation.
- [Use of] Results from defined internal quality control procedures in a single laboratory.
- [Use of] Results from collaborative studies
- [Use of] Results from proficiency test schemes used to assess the analytical competency of laboratories.

Ch 2: Uncertainty



- Definition and discussion of the concept of measurement uncertainty
- Comparison of 'error' and 'uncertainty'
- The VIM 3 definition of uncertainty

Ch. 3. Analytical Measurement and Uncertainty

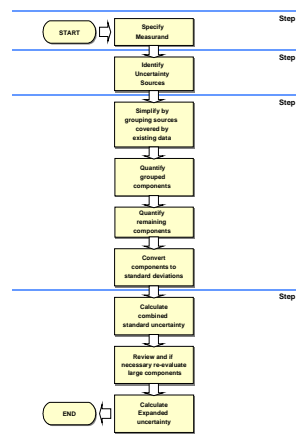


- Relationship of uncertainty and validation
- Conduct of experimental studies
- Traceability
- Traceability section reduced and referring to Eurachem/CITAC Traceability guide

Ch. 4. The Process of Measurement Uncertainty Estimation



- Outline of the process
 - Specify measurand
 - Identify Sources
 - Group and quantify
 - Combine
- Unchanged in 2012



Ch 5: Specification of the Measurand



- Improved statement of 'specification'
 - a statement of
 - a. the particular kind of quantity to be measured, usually the concentration or mass fraction of an analyte.
 - b. the item or material to be analysed and, if necessary, additional information on the location within the test item.
 - c. where necessary, the basis for calculation of the quantity reporting results.

- Taken from the Eurachem Guide to the VIM

Ch 6: Identifying Uncertainty Sources



- A list of likely sources of uncertainty

- Unchanged in 2012

Ch 7: Quantifying Uncertainty



- Introduction and procedure
- Evaluating uncertainty by quantification of individual components
- Closely matched certified reference materials
- Uncertainty estimation using prior collaborative method development and validation study data
- Uncertainty estimation using in-house development and validation studies
- Data from proficiency testing
- Empirical and ad-hoc methods

7.11ff: Quantification of individual components

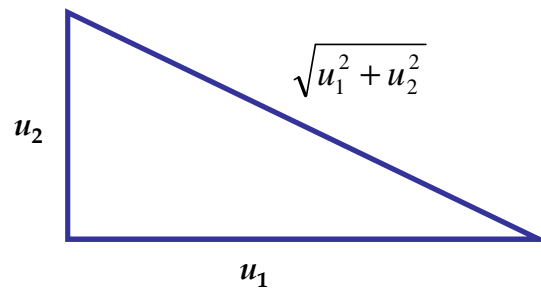


- Experimental estimation of individual uncertainty contributions
- Estimation based on other results or data
- Modelling from theoretical principles
- Estimation based on judgement
- Significance of bias
 - Unchanged, but Ch 2 notes VIM 3 reference to uncorrected bias in uncertainty estimates

CH 8: Combining uncertainties



- The basic GUM theory



- Adds cross-reference to simulation methods

Ch 9: Reporting uncertainties

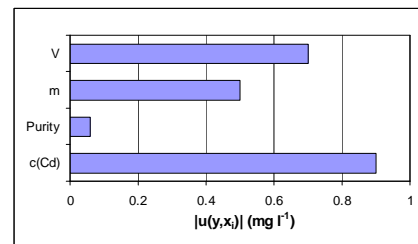
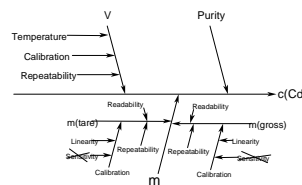


- Expanded uncertainty
- Interpretation against limits
 - Now references Eurachem Guide on “Use of uncertainty information in compliance assessment”

Appendix A: Examples



- Detailed worked Examples
- Summary provided for each
- All illustrate spreadsheet methods
- Some examples amended in revision



Appendices B-D



- A. Definitions
 - Reduced to simplify and refer to other guides
- B. Uncertainties in analytical processes
 - List of uncertainties
- C. Analysing uncertainty sources
 - Cause-and-effect analysis
 - Minor change to clarify

Appendix E: Useful Statistical Procedures

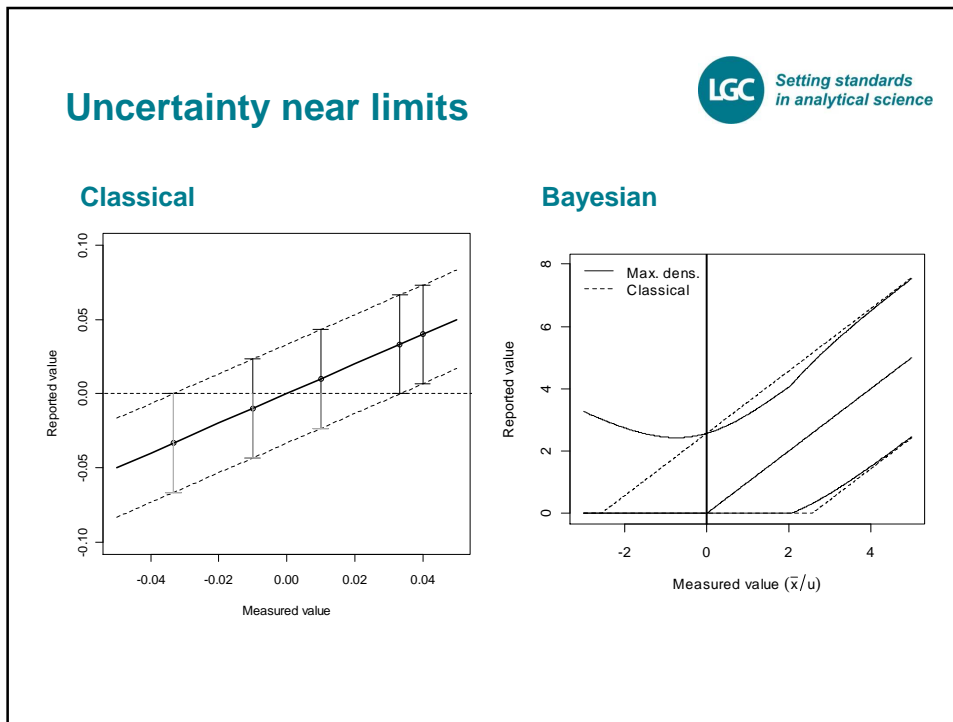


- Distribution functions
- Spreadsheet method for uncertainty calculation
- Evaluation of uncertainty using Monte Carlo simulation *New section*
- Uncertainties from linear least squares calibration
- Documenting uncertainty dependent on analyte level


Appendix F. Measurement uncertainty at the limit of detection/limit of determination



- Introduction
 - Observations and estimates
 - Validity of observations below zero
 - Reporting 'less than'/'greater than'
- Measurement uncertainty near zero
 - Expanded uncertainty intervals near zero: Classical approach
 - Expanded uncertainty intervals near zero: Bayesian approach *Substantial revision*



Appendices G, H

 *Setting standards
in analytical science*

- **G: Common sources and values of uncertainty**
 - Reference list to assist initial estimation
- **H: Bibliography**
 - Updated and with additional references

Summary



- A broad guide to measurement uncertainty estimation in analytical chemistry
- Covers basic GUM but also covers validation approaches thoroughly
- New sections on
 - Assessing compliance with limits
 - Uncertainty near detection limits
 - Monte Carlo methods