Uncertainty, asymmetry and constraints: Coverage intervals for large uncertainties

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Introduction

- The problem of large uncertainties
- Proportional uncertainty
- Uncertainty in results close to zero

The problem of large uncertainties

Setting standards in analytical science

- ISO Guide: Taylor expansion
  - Based on approximate linearity around x_i
  - Normality often a reasonable assumption
  - Accurate for small uncertainties
- Chemistry
  - Uncertainties can be large
  - Normality may not be an appropriate assumption

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How large is "large"?

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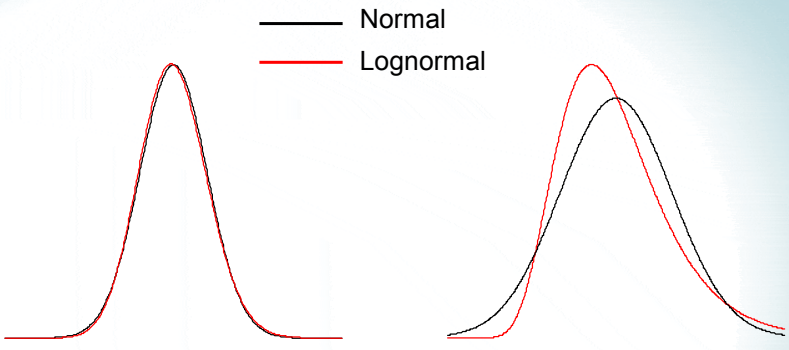

RSD = 0.05 RSD = 0.33

RSD < 0.1: Rarely a problem
RSD > 0.2: Cause for concern

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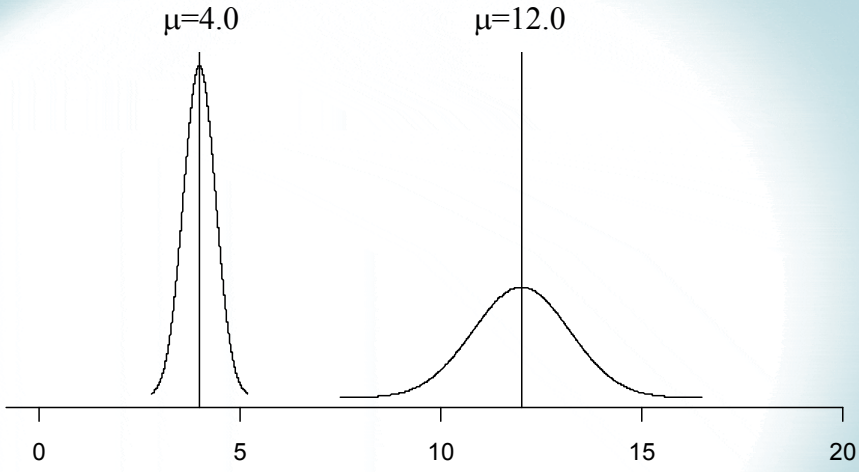
Proportional SD



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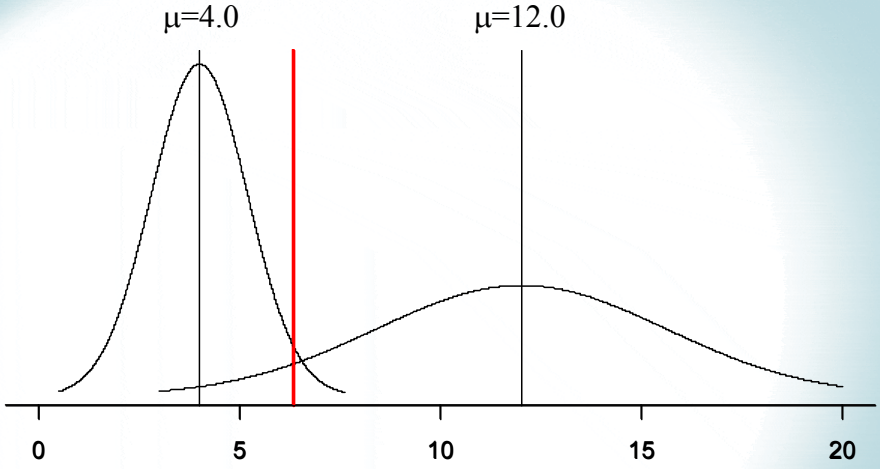
Proportional SD



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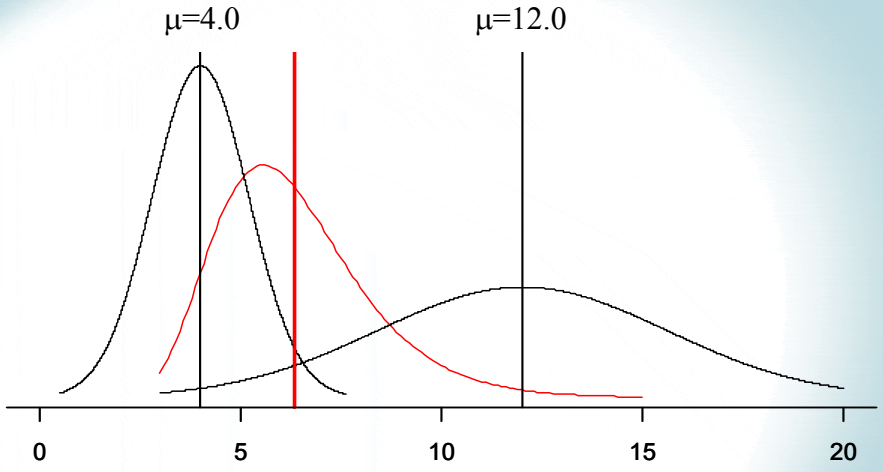
Proportional SD



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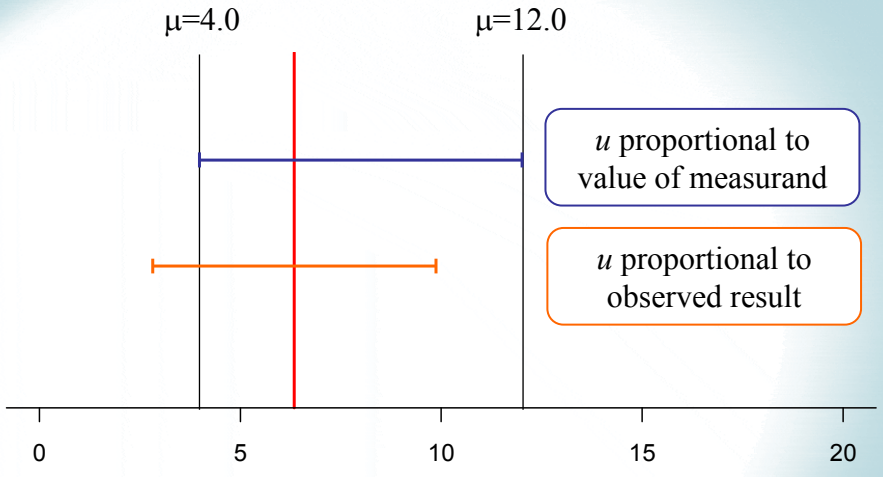
Proportional SD



u proportional to value of measurand

u proportional to observed result

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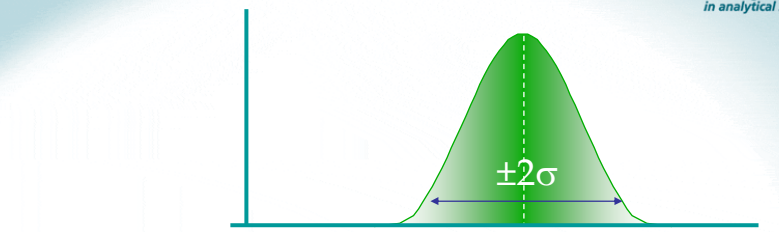
Implications of proportional SD

- The uncertainty about the value of the measurand (true analyte content) is non-normal
  - The confidence interval is asymmetric
- A good approximate decision point is obtained by
  - Estimating the uncertainty AT THE LOWER LIMIT
  - Calculating the decision point from the uncertainty associated with an observation exactly on the limit

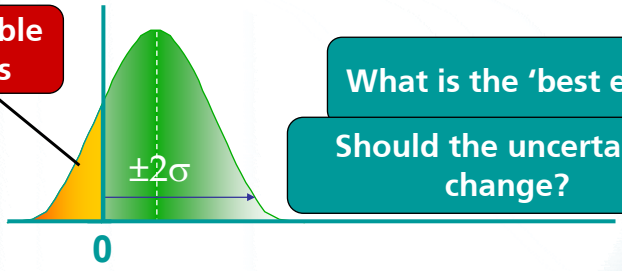
Uncertainties near zero

Uncertainty near zero/100%

Setting standards in analytical science



Impossible values



What is the 'best estimate'?

Should the uncertainty change?

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Truncation provides accurate coverage

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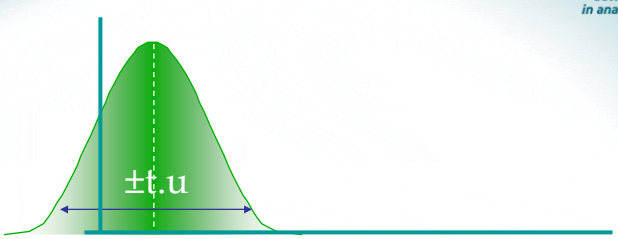

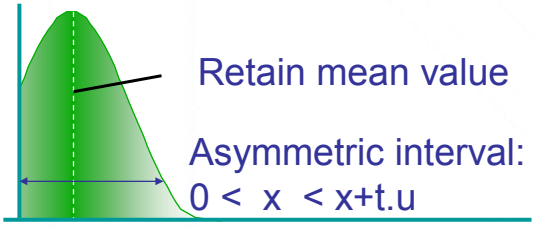

Retain mean value

Asymmetric interval:
0 < x < x+t.u

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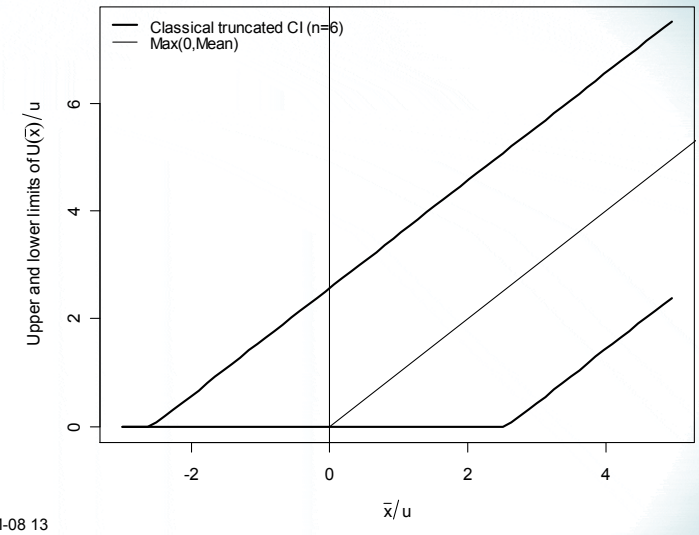
Truncated interval near zero



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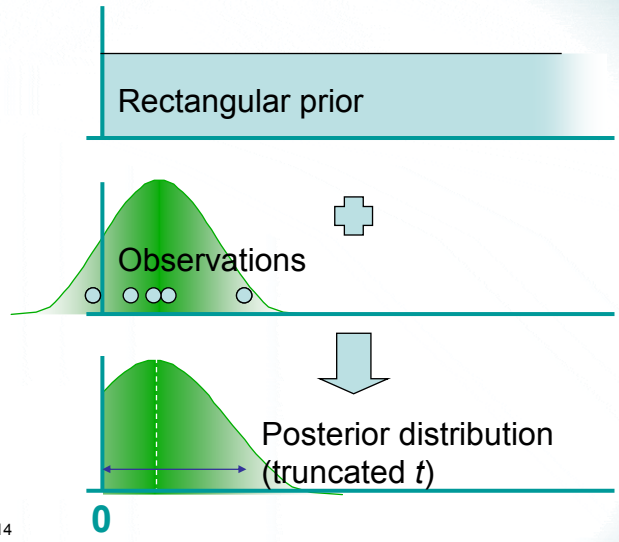
Bayesian approach



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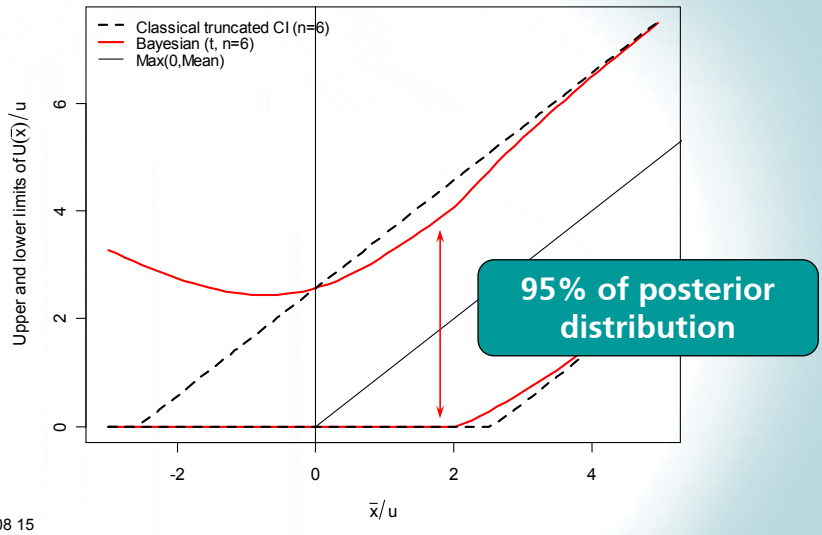
Bayesian interval



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Uncertainty on values near zero

- Truncated interval retains exact coverage properties
  - Standard uncertainty unchanged
  - Minimally biased mean
  - Convergence to zero width implies probable measurement failure
- Correct Bayesian interval more general but more complex to calculate
- Essential to truncate **AFTER ALL OTHER CALCULATIONS**
  - Truncating interim values leads to increased bias

"Handling undetected and low-level components in purity determination". S Cowen, S L R Ellison, Accred. Qual. Assur. ***12****, 323-328 (2007)*

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Summary

Setting standards in analytical science

- Uncertainty proportional to true value
  - base decision point on (symmetrical) distribution around the limit
- Uncertainties near zero
  - Calculate 2-sided confidence interval as usual
  - Truncate CI at zero
  - Report observed mean or zero (whichever is greater)

  OR
  - Use Bayesian interval
  - Report observed mean or zero (whichever is greater)