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Uncertainty evaluation based on practical examples – Why we need numerical methods

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Introduction

- **Uncertainty from a measurement equation**
- **Gradient methods**
  - Finite difference and Kragten's method
- **Simulation methods**
  - Monte Carlo simulation (MCS)
  - Bayesian approach using Markov chain Monte Carlo (MCMC)

Measurement equations

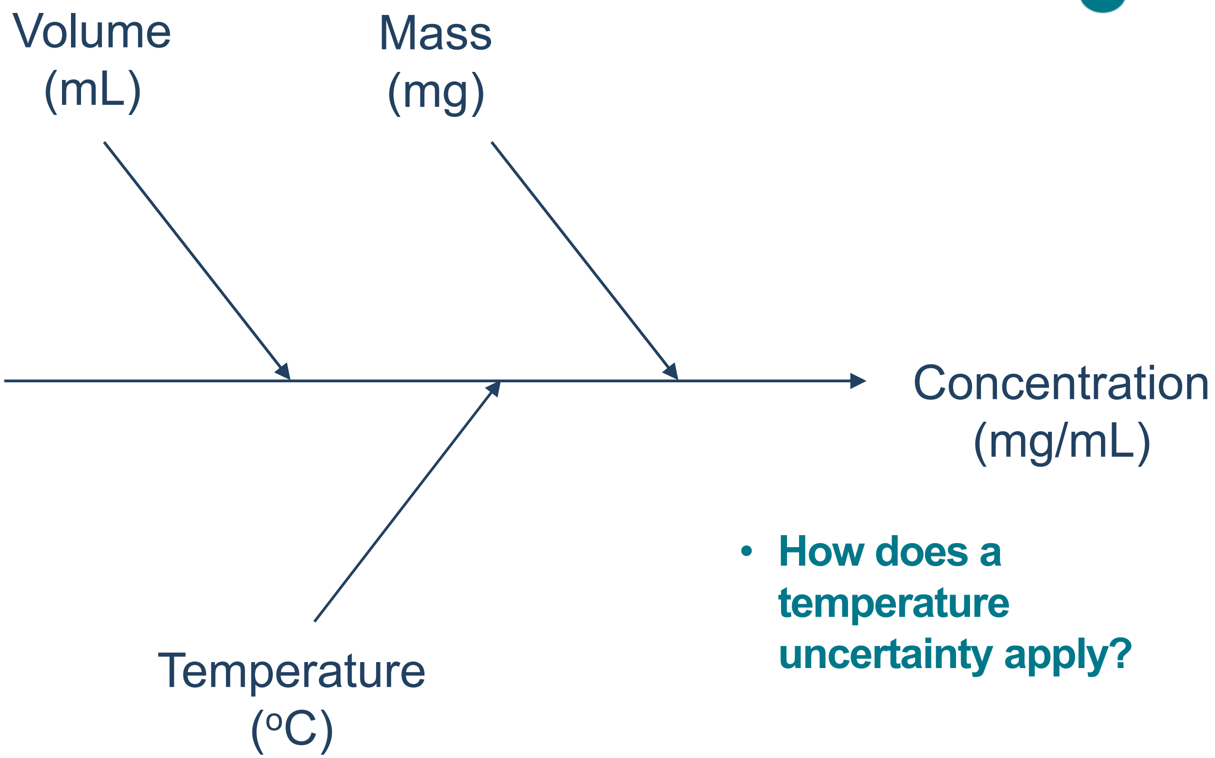
A simple example

A volumetric example

- Make up a 1 mg/ml solution
- in a 100ml volumetric flask (U = 0.2 ml, k=2)
- allowing for mass uncertainty (U = 4 mg, k=2)
- at a laboratory temperature 25 ± 2 °C

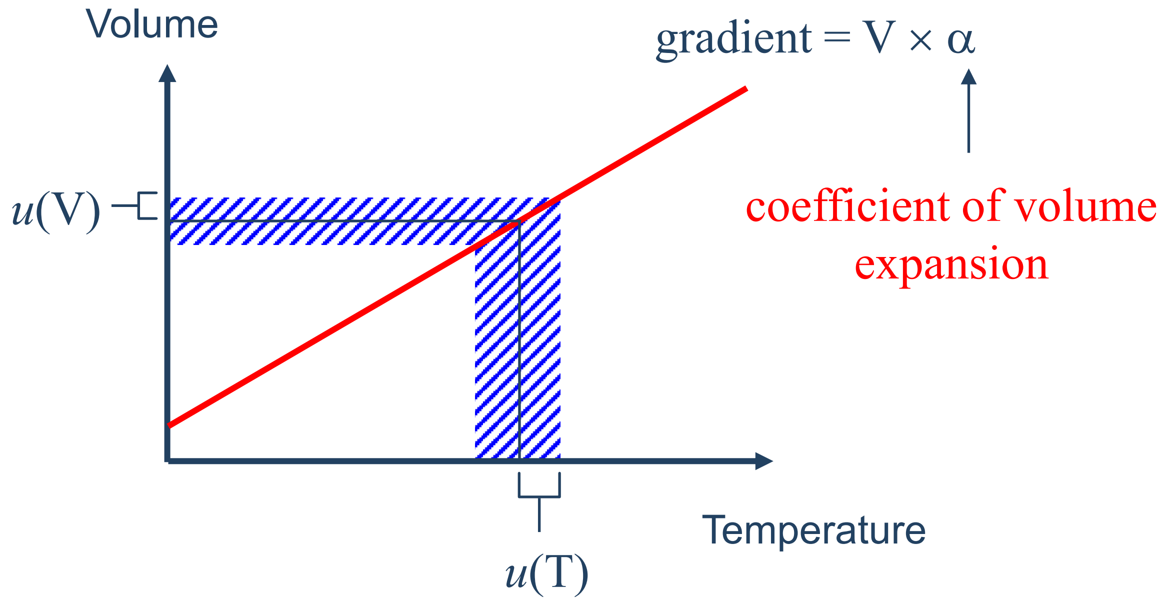
Evaluate the uncertainty in concentration

Example: The effect of temperature on concentration



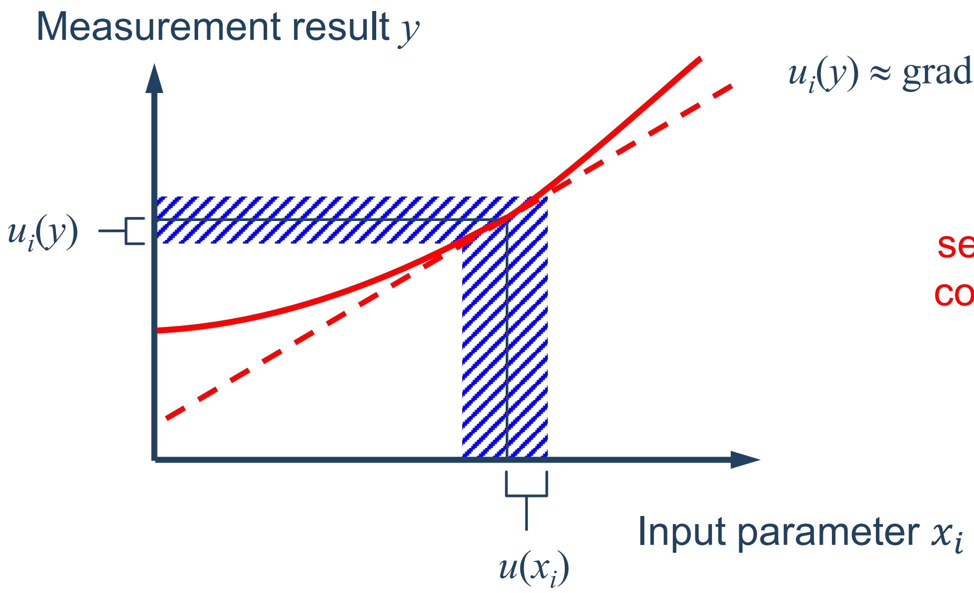
- **How does a temperature uncertainty apply?**

Example: The effect of temperature on volume



$u(V) = \text{gradient} \times u(T)$

Uncertainty propagation



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

sensitivity coefficient

Mathematical form of uncertainty

- x_i parameter affecting analytical result y
- $u(x_i)$ uncertainty in x_i
- $u_i(y)$ uncertainty in y due to uncertainty in x_i

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

↑ sensitivity coefficient

The volume example

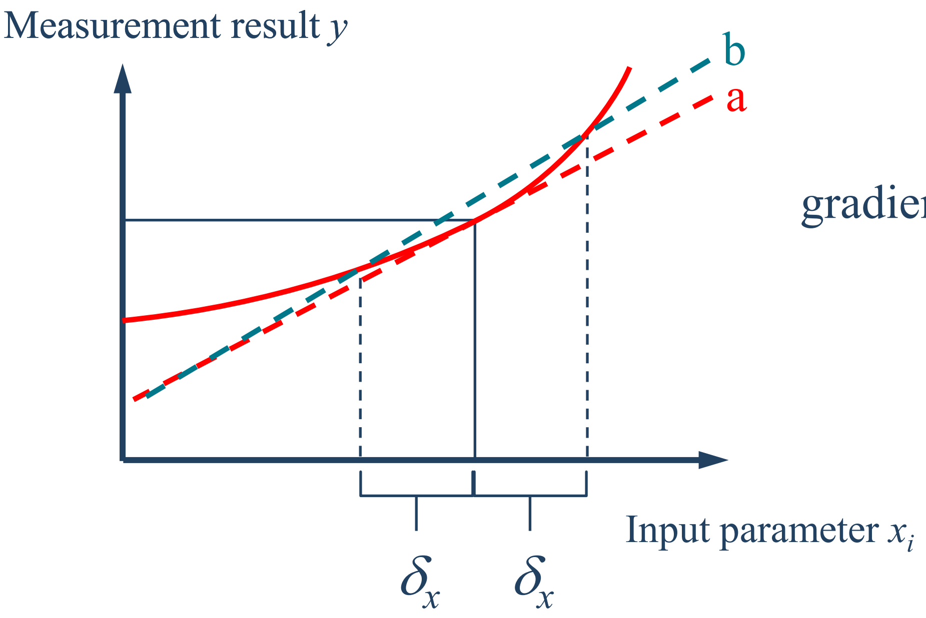
$$C_0 = \frac{m}{V_T}(1 + \alpha(T - T_0))$$

Quantity	Value x	Standard uncertainty u_x
Mass m	100 mg	2 mg
Volume V_T	100 ml	0.1 ml
Volume coefficient α	1×10^{-3} K^{-1}	
Temperature T	25 °C	1.15 °C
Standard temperature T_0	25 °C	

Sensitivity coefficients from spreadsheets

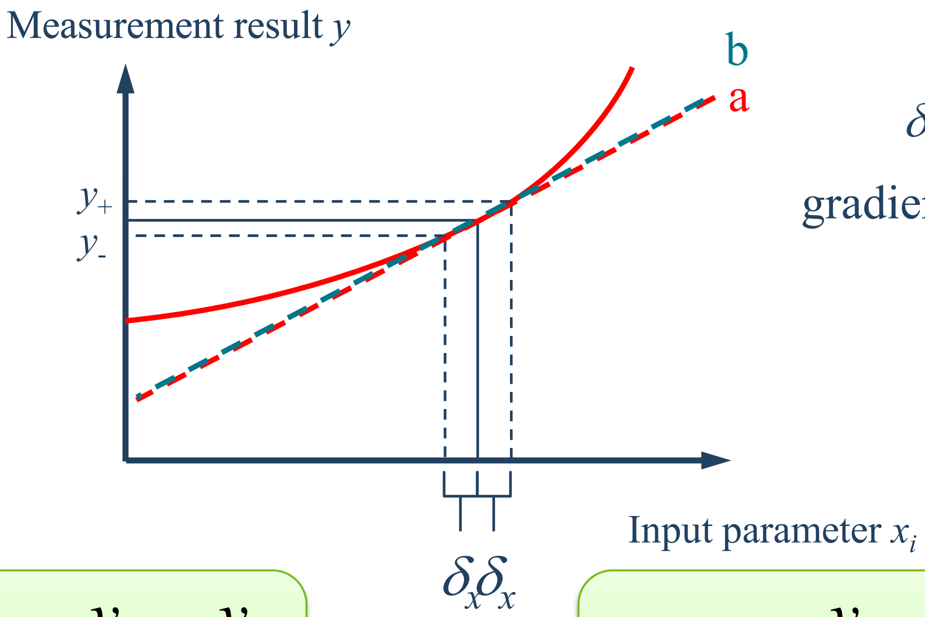
1. Differentiation by finite difference

Finite difference method



gradient(b) ≈ gradient(a)

Finite difference method



$\delta_x \rightarrow 0$

gradient(b) $\rightarrow$ gradient(a)

$$\frac{\partial y}{\partial x_i} \approx \frac{y_+ - y_-}{2\delta_{x_i}}$$

$$u_i(y) \approx \frac{y_+ - y_-}{2\delta_{x_i}} u(x_i)$$

Compare finite difference with the GUM

GUM first order

Uncertainty budget:

	x	u	c	u.c
m	100	2.0	0.01	0.02
V_T	100	0.10	-0.01	0.001
T	25	1.15	-0.001	0.00115

y: 1

u(y): 0.20

Finite Difference ($\delta = 0.01u$)

Uncertainty budget:

	x	u	c	u.c
m	100	2.0	0.01	0.02
V_T	100	0.10	-0.01	0.001
T	25	1.15	-0.001	0.00115

y: 1

u(y): 0.20

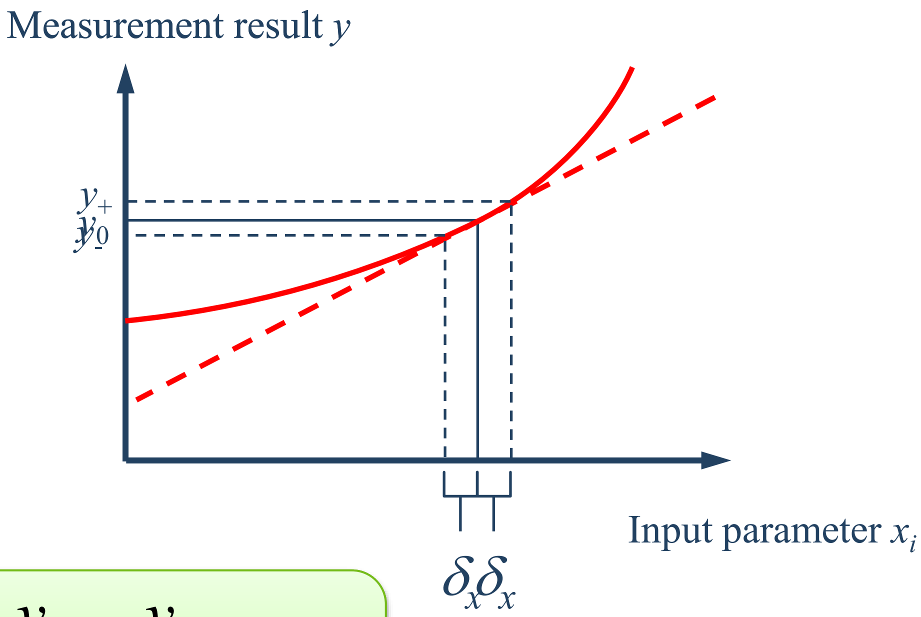
Disadvantages of the finite difference method

- **Two additions and a division**
  - Slightly tedious in a spreadsheet
- **No obvious choice of δ**
  - Big enough to avoid internal round-off errors
  - Small enough for a ‘good’ approximation
  - Can take several trial runs to establish reliable difference

Sensitivity coefficients from spreadsheets

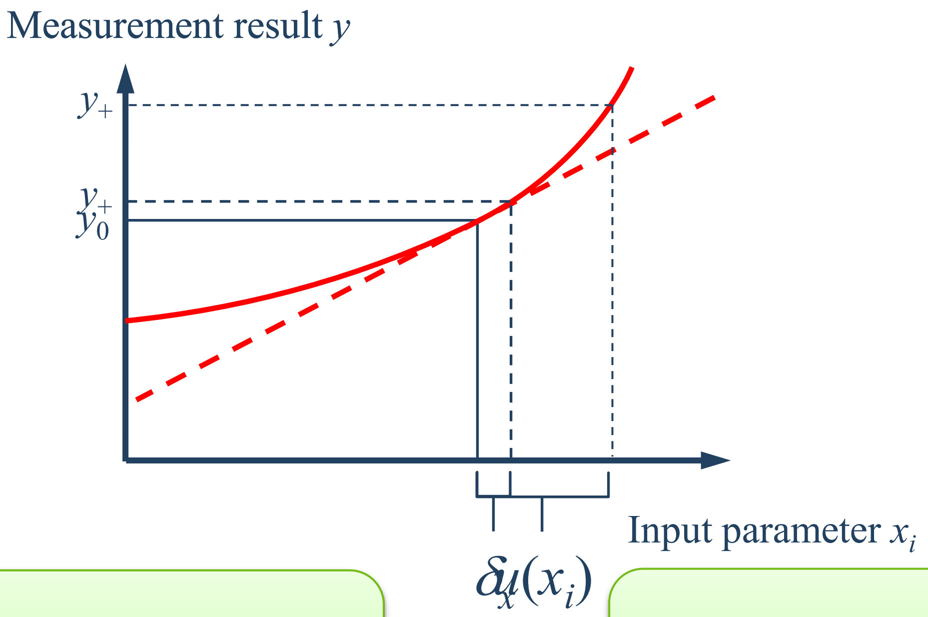
2. Kragten's method

Kragten's method



$$u_i(y) \approx \frac{y_+ - y_0}{\delta_{x_i}} u(x_i)$$

Kragten's method



$$u_i(y) \approx \frac{y_+ - y_0}{u(x_i)} u(x_i)$$

$$u_i(y) \approx y_+ - y_0$$

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:2012

WARNING

Kragten is not exact for non-linear cases

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Compare Kragten with FD

Finite Difference

Expression: a/(b - c)

Uncertainty budget:

	x	u	c	u.c
a	1	0.05	1.000000	0.0500000
b	3	0.15	-1.000002	-0.1500003
c	2	0.10	1.000001	0.1000001

y: 1.0

u(y): 0.1870832

Kragten

Expression: a/(b - c)

Uncertainty budget:

	x	u	c	u.c
a	1	0.05	1.0000	0.05000
b	3	0.15	-0.8695	-0.13043
c	2	0.10	1.1111	0.11111

y: 1.0

u(y): 0.1784906

Why would we use a *less* accurate algorithm?

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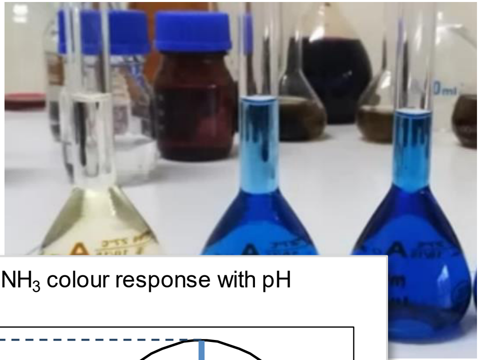
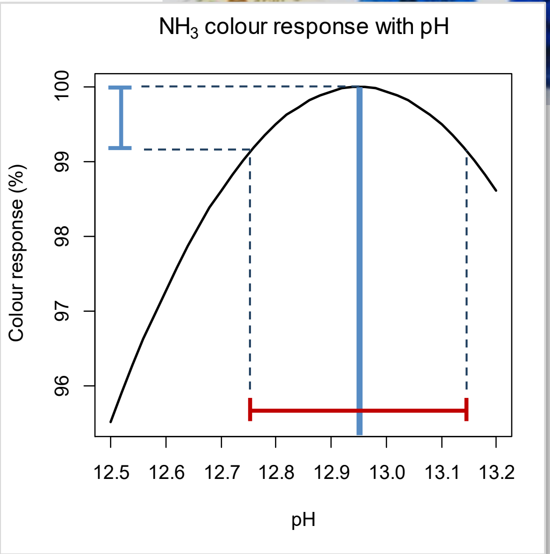
Example: Ammonia in water

- Spectrophotometric determination
- Phenol/hypochlorite forms indophenol blue; enhanced with sodium nitroprusside and measured photometrically





- Colour formation is pH-sensitive*
- Analysis may be carried out close to maximum
- Require MU due to pH uncertainty

* Pym, R. V. E., Milham, P. J., Analytical Chemistry, 1976, 48, 9, 1413-1415

(NH_3) example: Kragten vs GUM

GUM

Expression: a * pH^2 + b * pH + c

Uncertainty budget:

	x	u	c	u.c
pH	12.95	0.115	0.0000	0
a	-22.22	0.000	167.7025	0
b	575.56	0.000	12.9500	0
c	-3626.72	0.000	1.0000	0

y: 100

u(y): 0.0

Kragten

Expression: a * pH^2 + b * pH + c

Uncertainty budget:

	x	u	c	u.c
pH	12.95	0.115	-2.57	-0.2963
a	-22.22	0.00	167.70	0.0
b	575.56	0.00	12.95	0.0
c	-3626.72	0.00	1.00	0.0

y: 100

u(y): 0.296

Finite difference methods compared

Finite difference 1st order

- Accurate gradient
- Faithfully reproduces 1st order GUM uncertainty
- Simple to calculate

- 1st order GUM is insufficient for highly non-linear cases
  - Needs 2nd and higher order

Kragten

- Exact only for linear examples
- Does not reproduce 1st order GUM
- Simple to calculate

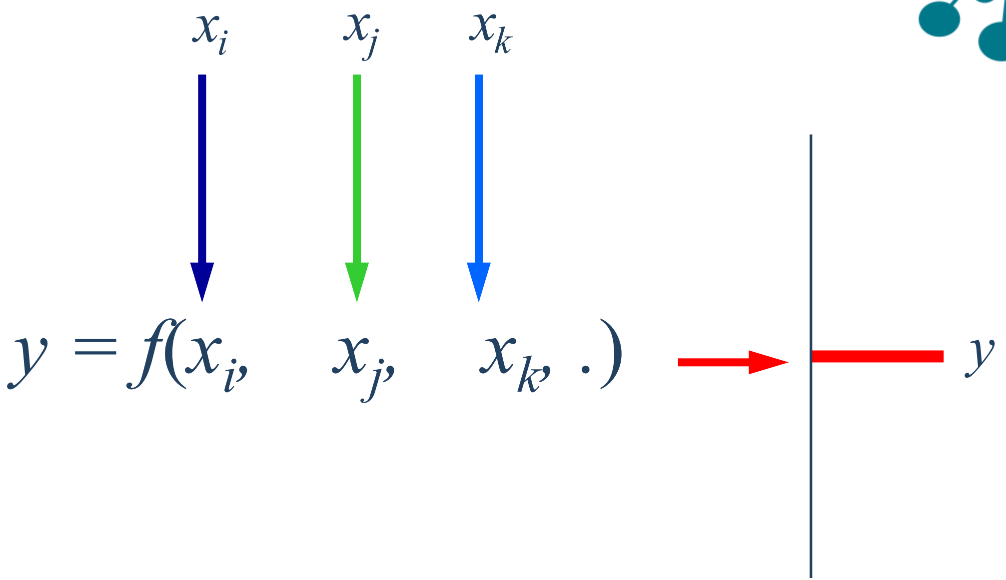
- Usually adequate for mild nonlinearity
- May be better for highly non-linear cases

Both much simpler than manual differentiation

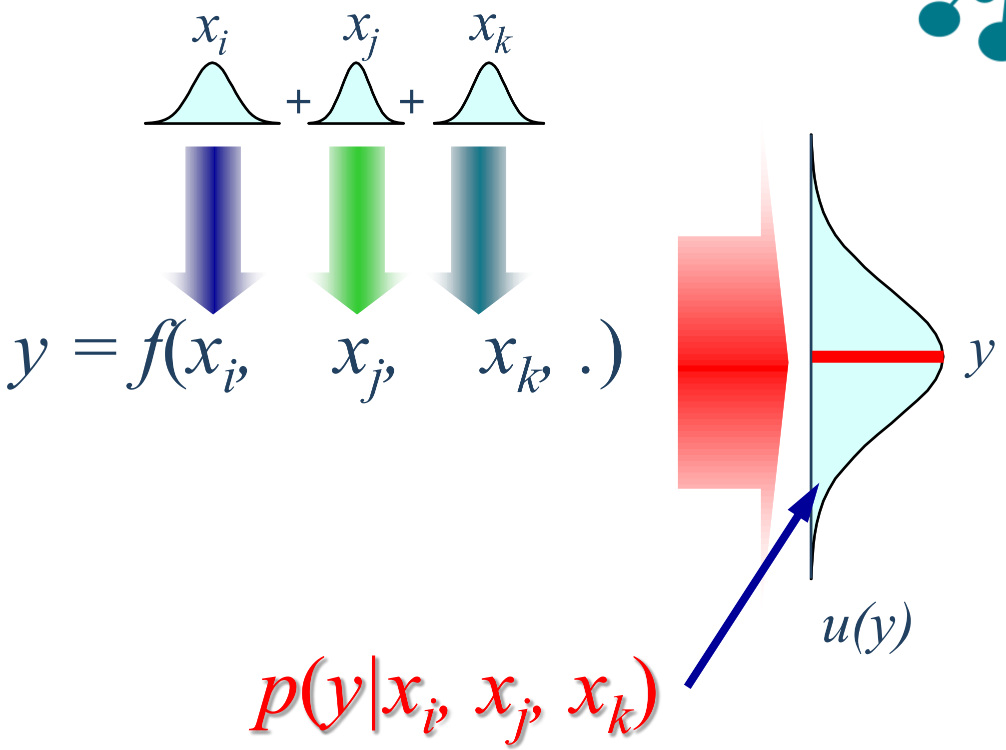
Simulation methods

1. Monte Carlo Simulation
   (GUM Supplement 1)

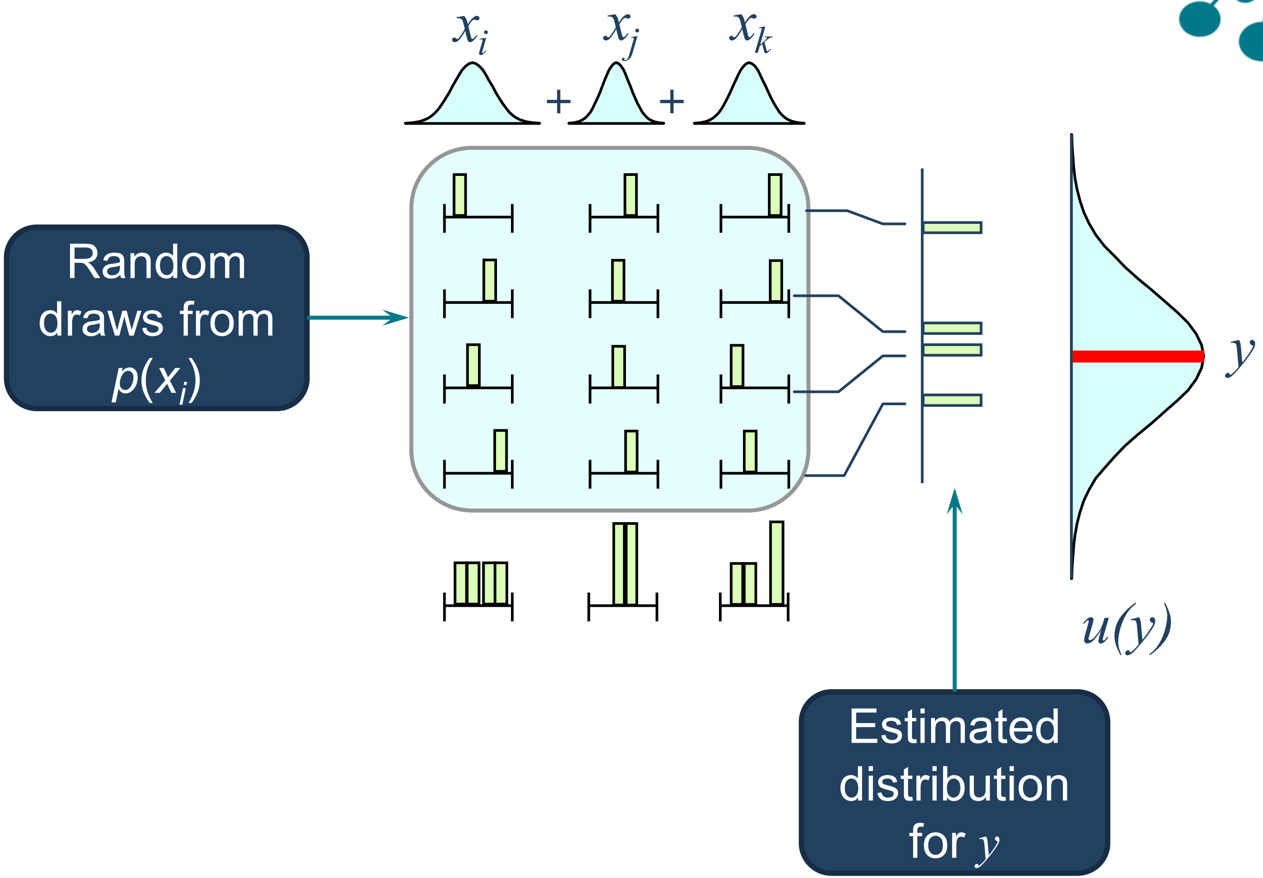
Principle of simulation



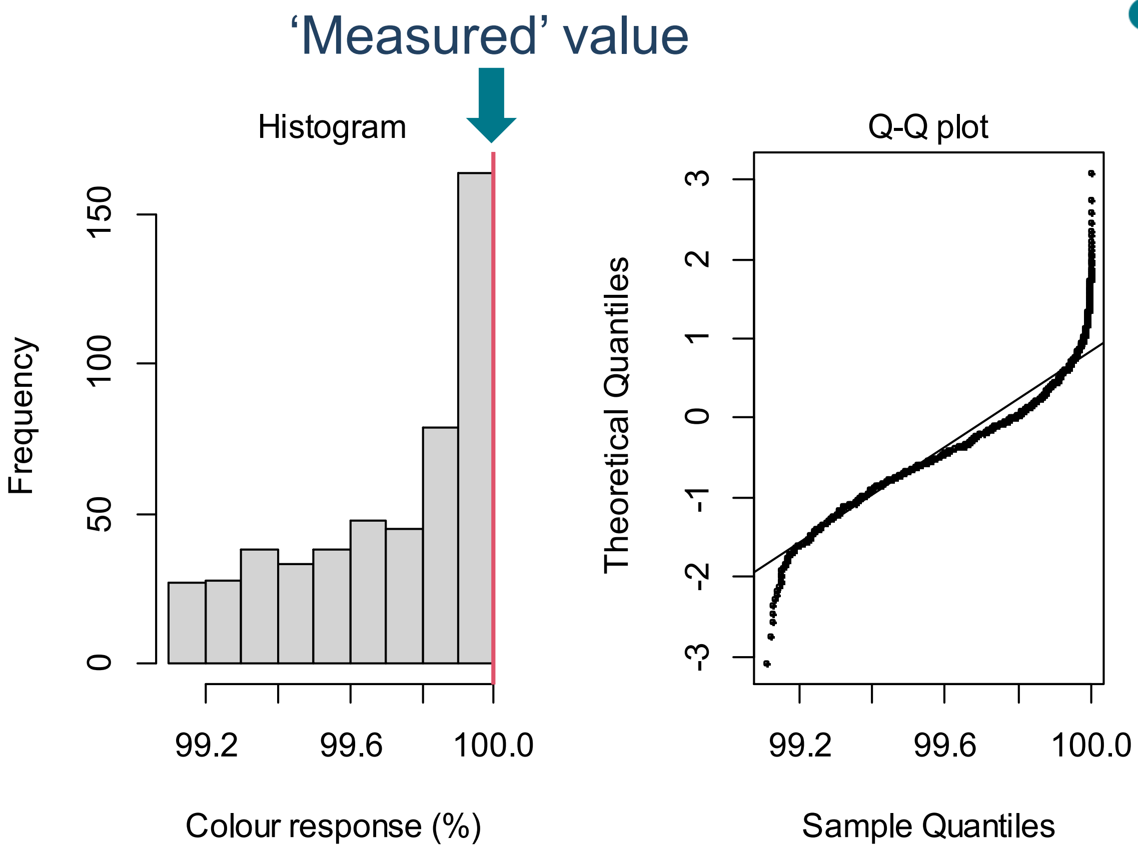
Principle of simulation



Principle of simulation



NH_3 example: MCS, 500 replicates



Calculations carried out using metRology 0.9-29 (http://sourceforge.net/projects/metrology/)

(NH_3) example: MCS and Kragten

MCS

Expression: a * pH^2 + b * pH + c

Uncertainty budget:

	x	u	c	u.c
pH	12.95	0.115	0.049	-0.0056

distrib	distrib.pars
unif	min=12.75, max=13.15

y: 100
u(y): 0.265

Kragten

Expression: a * pH^2 + b * pH + c

Uncertainty budget:

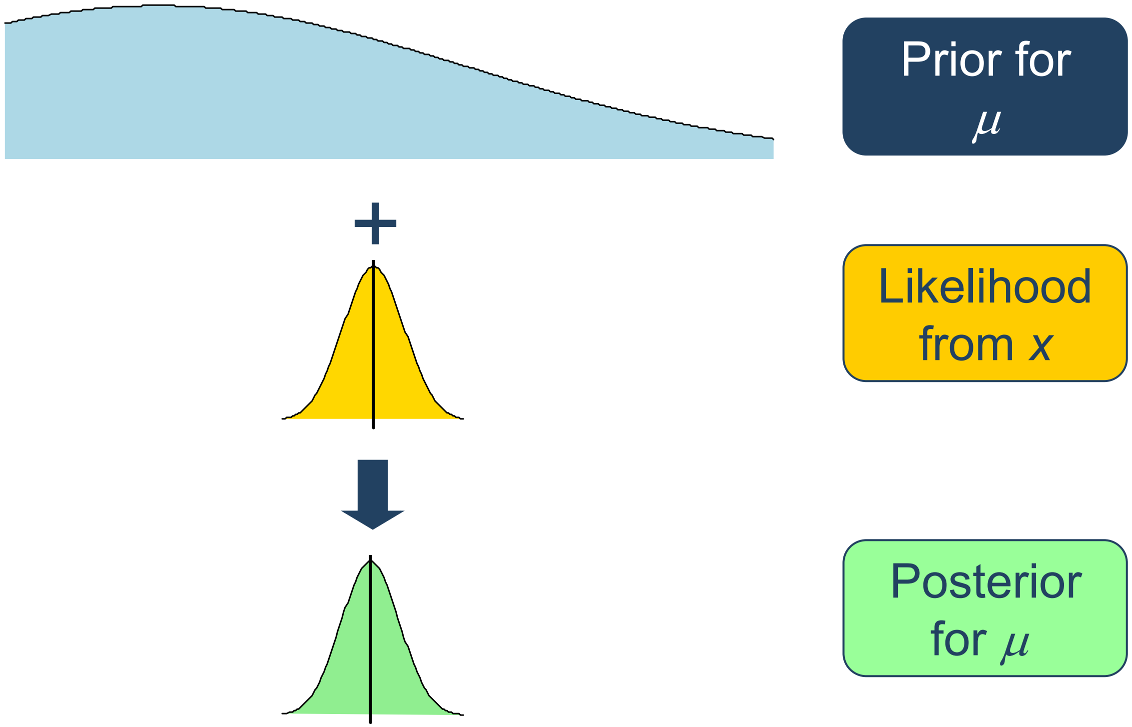
	x	u	c	u.c
pH	12.95	0.115	-2.57	-0.2963
a	-22.22	0.00	167.70	0.0
b	575.56	0.00	12.95	0.0
c	-3626.72	0.00	1.00	0.0

y: 100
u(y): 0.296

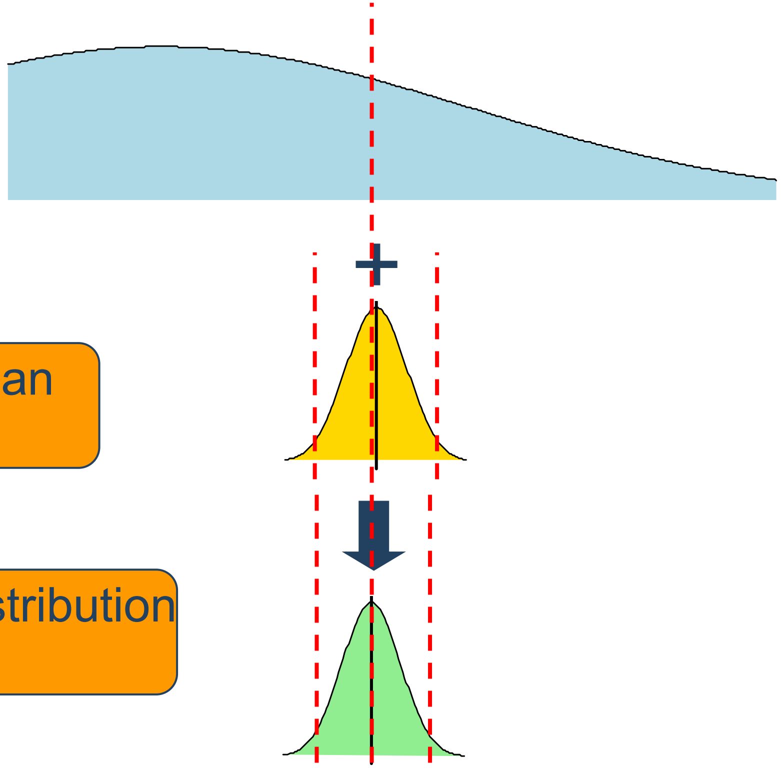
Simulation methods

2. Bayesian methods using MCMC

Bayes applied to Measurement Uncertainty



Bayes applied to Measurement Uncertainty



Prior for μ

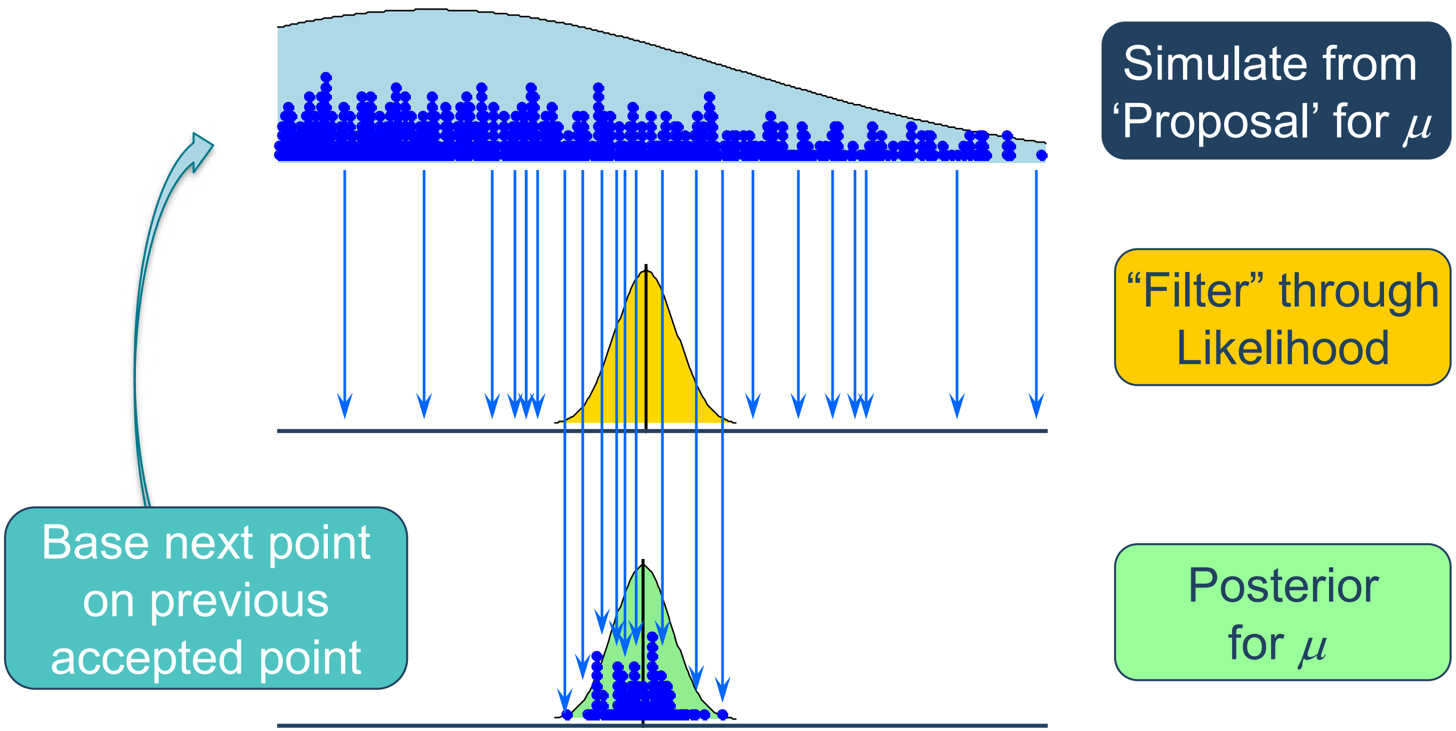
Likelihood from x

i) The mean shifts

ii) The distribution differs

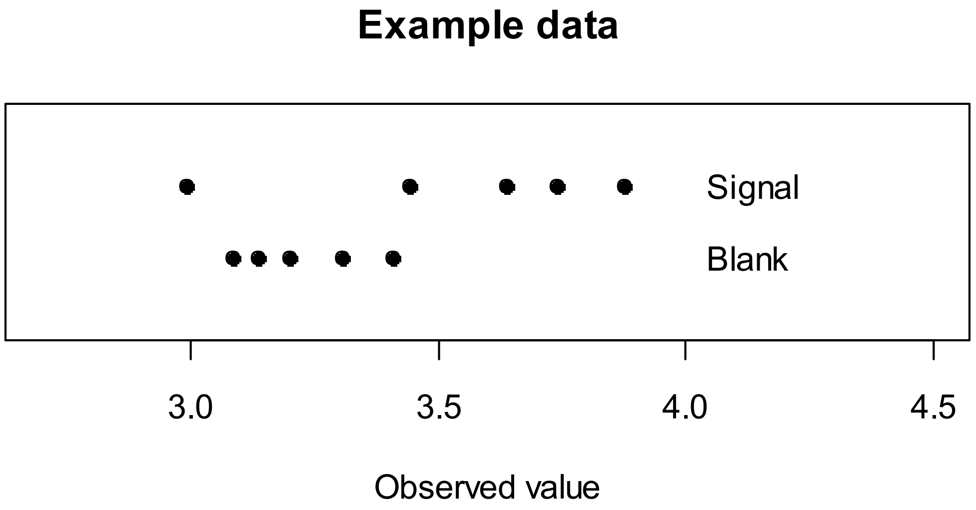
Posterior for μ

Bayes via Markov Chain Monte Carlo (MCMC)



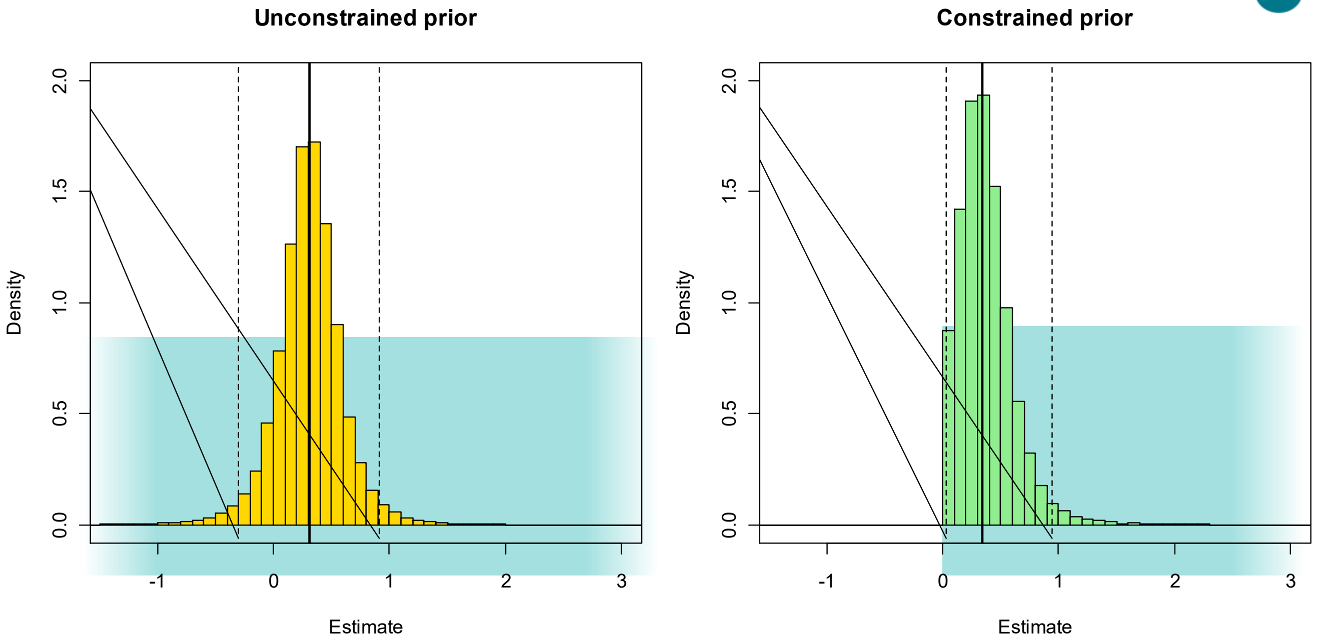
MCMC example

- *y* is a concentration calculated from a signal minus a blank value



- True concentration cannot be below zero

MCMC example - results



Uniform priors assumed for *y* and for both variances; error distributions assumed normal.

Calculations carried out using WinBUGS 1.4

Bayes is useful with informative prior information

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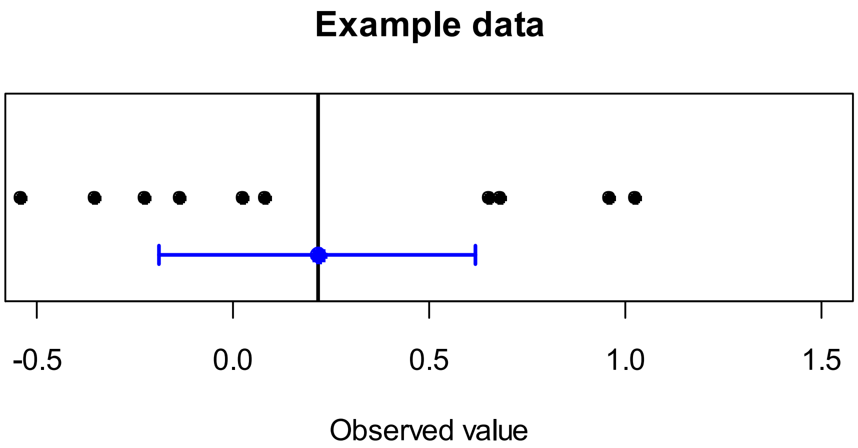
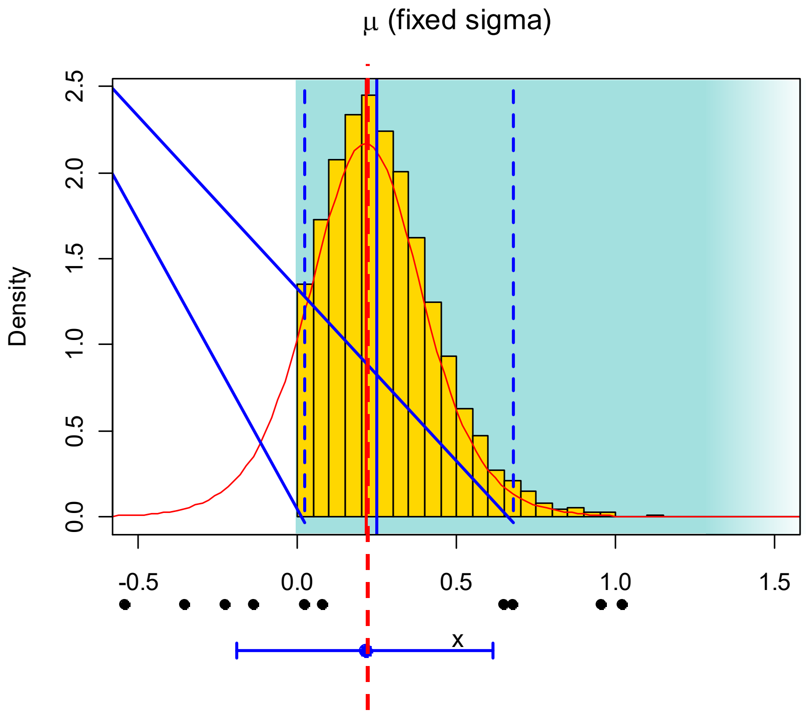
MCMC example 2:
Constant RSD - SD proportional to μ

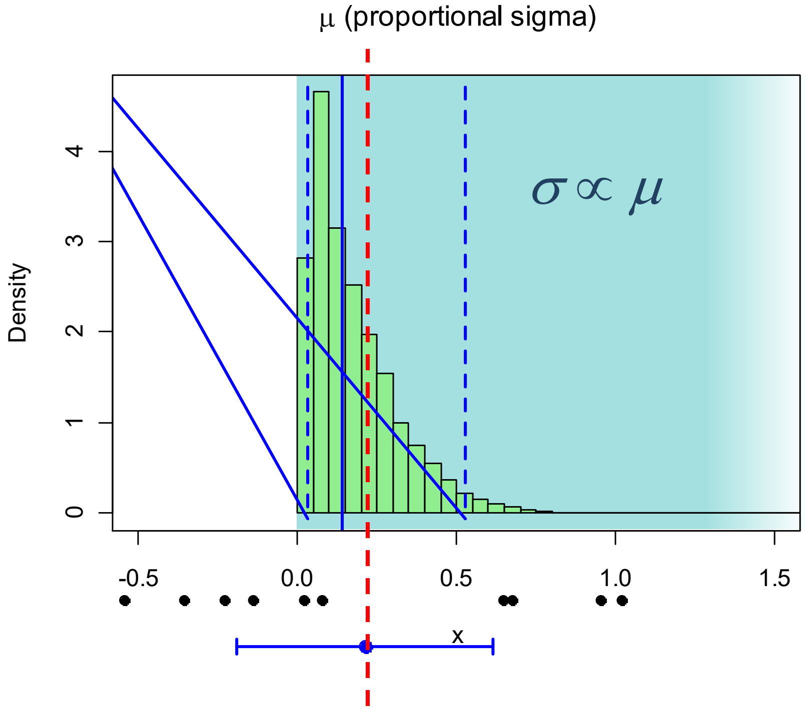


- **Concentration: not below zero**
- **Common observation: standard deviation proportional to true value**

MCMC results:
i) Fixed standard deviation



MCMC results
ii) Proportional standard deviation



Bayes respects the underlying statistical model

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Bayes and measurement uncertainty: Avoiding controversy

Rule 1: The default: Use an uninformative prior

- typically wide Normal or Uniform

Rule 2: There are no truly uninformative priors

- And some ‘uninformative’ priors can be unexpectedly informative

Rule 3: If an uninformative prior works for measurement uncertainty, there’s probably an easier way

Bayes theorem is most useful for *uncontroversial, informative* priors

Summary

- **Numerical methods work**
  - when used with care
- **Finite difference and Kragten methods are simple to calculate and usually reliable**
  - Kragten's method less like 1st order – but this is often good!
- **Simulation methods show distributions**
  - Not just standard uncertainties
- **MCS (GS1) simple but computer intensive**
- **MCMC more appropriate for constraints and *x* distribution dependent on *y* (eg proportional sd) .. BUT:**
  - Much more difficult – specialist software only
  - Interpretation needs care

Software

- **Simple MCS, Kragten and Finite Difference**
  - metRology version 0.9-4 running under R version 2.12
  - *http://sourceforge.net/projects/metrology*

- **Bayesian MCMC calculation**
  - WinBUGS
    http://www.mrc-bsu.cam.ac.uk/bugs/winbugs/contents.shtml
  - Stan[2]
    https://mc-stan.org/

- **See also**
  - JAGS[1]
    https://mcmc-jags.sourceforge.io/