

In the Final Analysis

The 2006 L S Theobald Lecture

delivered at the University of Plymouth
on 03/05/06 by

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The three essentials of quality

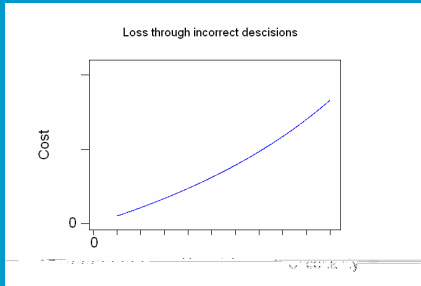
- What accuracy does the customer **NEED**?
Fitness for purpose (Decision theory)
- What accuracy **CAN** I achieve?
Single laboratory validation
Collaborative trials
- What accuracy **DO** I achieve?
Internal quality control
Proficiency testing

Three issues relating to quality

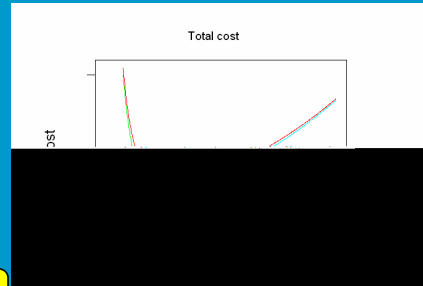
- Fitness for purpose (What is it?)
- Statistics (Can we do it?)
- Metrology (Do we need it?)



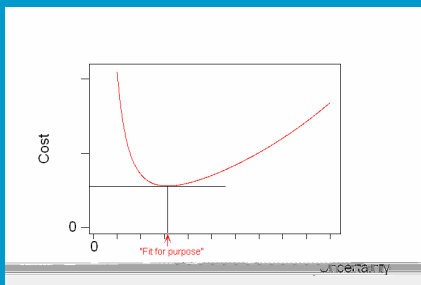
Typical loss function



Long-term loss



Fit-for-purpose uncertainty



Balancing sampling and analytical uncertainties

$$u = \sqrt{u_{sam}^2 + u_{an}^2} \quad u_{sam} = u_{an} ?$$

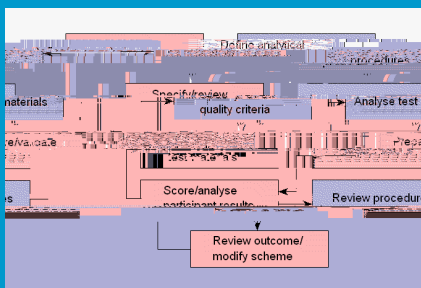
$$\frac{u_{an}}{u_{sam}} = \frac{L_{sam}}{L_{an}}^{1/4}$$

L_{sam} , L_{an} are unit costs for a given uncertainty.

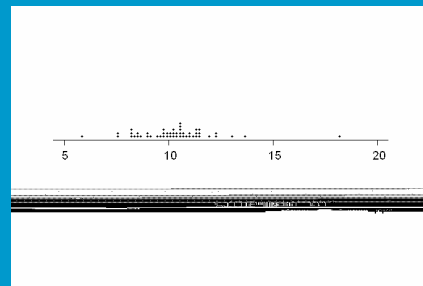
Fearn et al, *Analyst*, 2002, **127**, 818-824.
AMC Technical Brief No. 20.

Proficiency tests - organisation

Provider Participant



Participants' raw results



The z-score

$$z = (x - x_a) / s$$

x = participant's result;

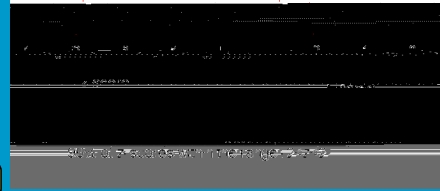
x_a = the "assigned value", the scheme provider's best estimate of the true value;

s = the "standard deviation for proficiency", a scaling factor.



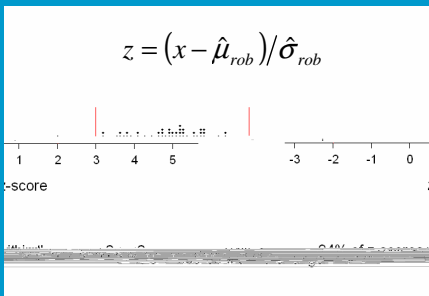
Using simple statistics for x_a and s

$$z = (x - \bar{x}) / s$$



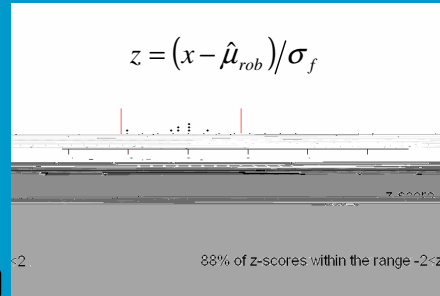
Using robust statistics

$$z = (x - \hat{\mu}_{rob}) / \hat{\sigma}_{rob}$$



Using a fitness-for-purpose criterion σ_f

$$z = (x - \hat{\mu}_{rob}) / \sigma_f$$



rob



$$\mathbf{x}^T = [x_1 \ x_2 \ \dots \ x_n]$$

Set $1 < k < 2$, $p = 0$, $\hat{\mu}_0 = \text{median}$, $\hat{\sigma}_0 = 1.5 \times \text{MAD}$

$$\begin{array}{ll} x_i & \mu_p - k\sigma_p < x_i < \mu_p + k\sigma_p \\ x_i = \mu_p - k\sigma_p & x_i < \mu_p - k\sigma_p \\ \mu_p + k\sigma_p & x_i < \mu_p + k\sigma_p \end{array}$$



The normal kernel density

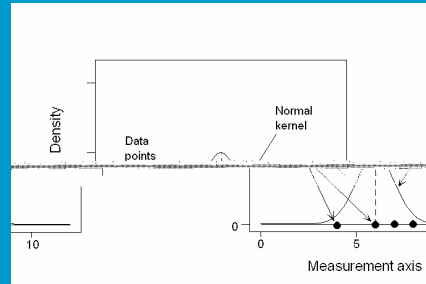
$$y = \frac{1}{nh} \sum_{i=1}^n \Phi \frac{x - x_i}{h}$$

where Φ is the standard normal density,

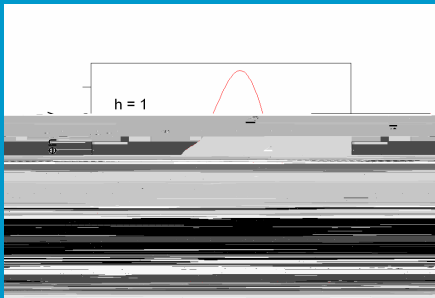
$$\Phi(a) = \frac{\exp(-a^2/2)}{\sqrt{2\pi}}$$

AMC Technical Brief No. 4

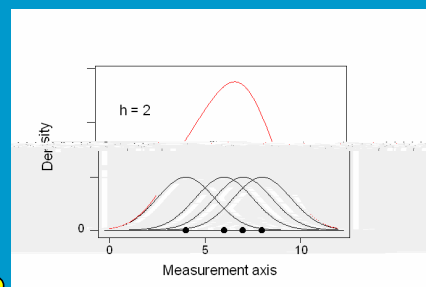
A normal kernel



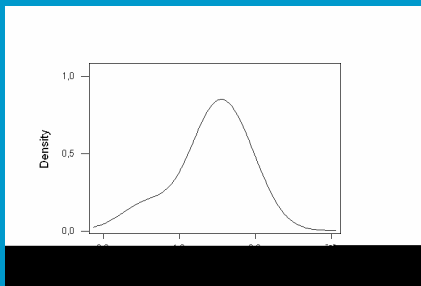
A kernel density



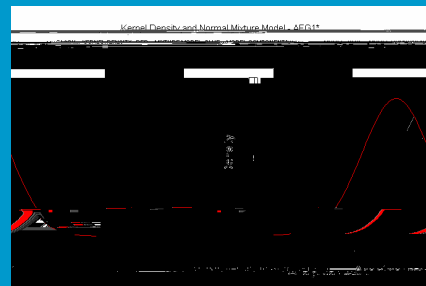
Another kernel density



Kernel density of the aflatoxin data



“Fit” of normal model



The normal mixture model

$$f(y) = \sum_{j=1}^m p_j f_j(y), \quad \sum_{j=1}^m p_j = 1$$

$$f_j(y) = \frac{\exp(-(y - \mu_j)^2 / 2\sigma^2)}{\sqrt{2\pi}\sigma}$$



AMC Technical Brief No 23, and AMC Software. Thompson, *Acc Qual Assur*, 2006, **10**, 501-505.

Mixture models found by the maximum likelihood method (the EM algorithm)

- The M-step

$$\hat{p}_j = \frac{\sum_{i=1}^n \hat{P}(j|y_i)}{n}$$

$$\hat{\mu}_j = \frac{\sum_{i=1}^n y_i \hat{P}(j|y_i)}{\sum_{i=1}^n \hat{P}(j|y_i)}$$

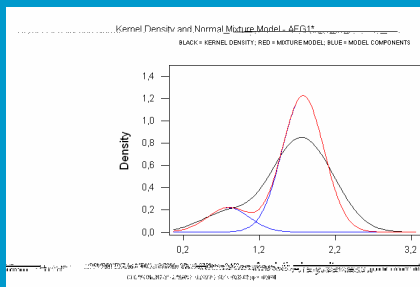
$$\hat{\sigma}^2 = \frac{\sum_{j=1}^m \sum_{i=1}^n (y_i - \hat{\mu}_j)^2 \hat{P}(j|y_i)}{\sum_{j=1}^m \hat{P}(j|y_i)}$$

- The E-step

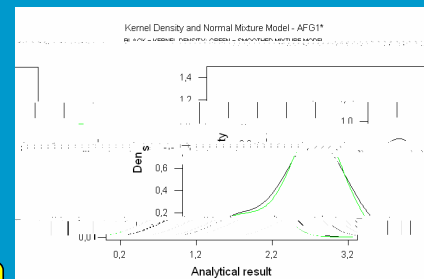
$$\hat{P}(j|y_i) = \frac{\hat{p}_j f_j(y_i)}{\sum_{j=1}^m \hat{p}_j f_j(y_i)}$$



Kernel density and fit of 2-component normal mixture model



Kernel density and variance-inflated mixture model



Find out more?

AMC Technical Briefs and Software on
www.rsc.org/amc/

Statistics

- Lies, damned lies, and statistics!

Metrology

- Fiction, science fiction, and metrology!

Metrologist's creed

- Uncertainty is important.
- Analytical chemists are not good at estimating uncertainty.
- All results of chemical measurement are traceable to SI units, in particular the mole, the kilogramme, the metre.
- Analytical chemists don't worry about traceability, that's why their results are questionable.

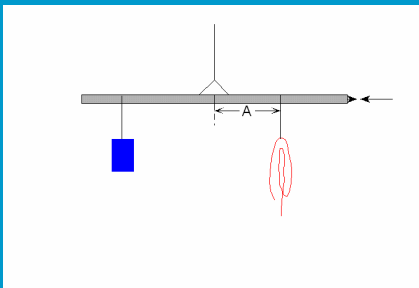


Metrological false premise 1

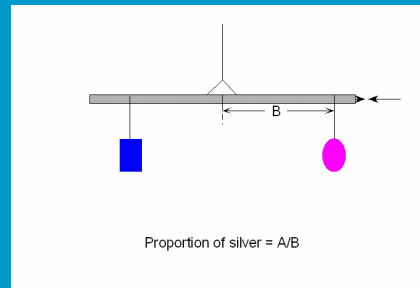
- All analytical results are traceable to SI units, in particular the mole, the kilogramme, and the metre.
- *NO!* The majority of analytical measurements made for commercial purposes are mass fractions, not traceable to *any* unit.
Corollary: expressions such as %, ppm, ppb, etc are perfectly correct.



False premise No 1 contd. – Silver content of silver solder



False premise No 1 contd. – Silver content of silver solder



False premise No 1 contd. – Silly or what!

- Is the concentration of silver, A/B , traceable to the metre?
- Should we express the result as (say) 70 cm m^{-1} ?
- Or 700 mg g^{-1} (when no mass standard is involved)?



Metrological false premise 2

- Chemical measurement results are not accurate enough, and that is because of a lack of traceability to SI units.
- *NO!* Most chemical measurement results are fit for purpose or more accurate.
- Where results are not accurate enough—it sometimes happens—the shortfall is often irreducible and traceability to SI units does not help.

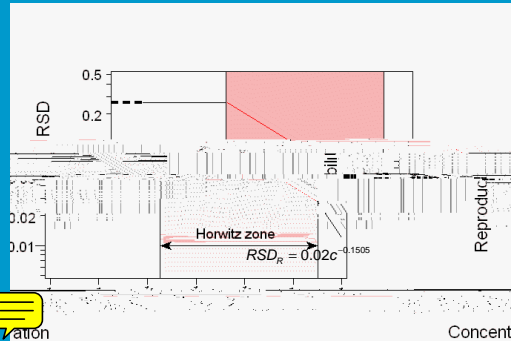


Metrological false premise 3

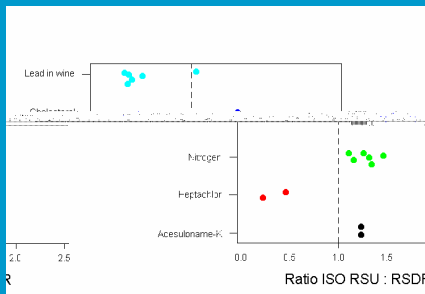
- Uncertainty is under-estimated by interlaboratory studies: only “bottom-up” models with clear traceability to SI units give the correct answer.
- **NO!** When proper comparisons are made, we mostly find that (say) reproducibility standard deviations from collaborative trials give equal or greater uncertainty estimates than “bottom-up”.



Reproducibility relative standard deviations

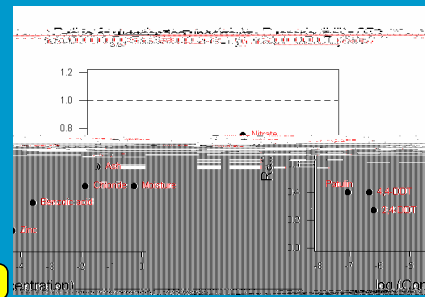


“Top-down versus bottom-up”

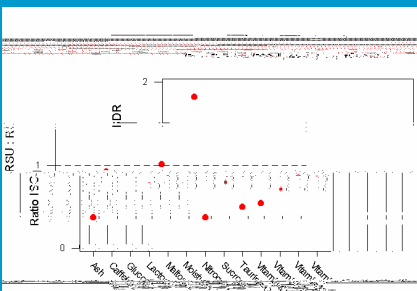


Thompson *et al* data

Analyst, 2002, 117, 1669-1675.



Populaire & Giménez data



Metrological false premise 4

- Chemical measurements have a larger relative uncertainty in comparison with most physical measurements. (True)
- That is because they are not traceable to SI units.
- **NO!** The traceability chain to SI units contributes almost nothing to the combined uncertainty of analytical results.

Metrological false premise 4 contd.

- Realistic relative uncertainties in analytical results are mostly in the approximate range 1-30%.
- Relative uncertainties in transferring SI units (such as mass and volume) to the analytical laboratory bench are less than 0.1%.

Metrological false premise 5

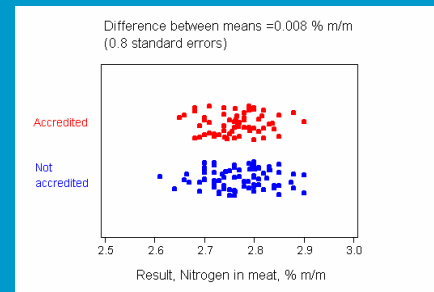
- Terms such as “true value”, “trueness”, and “bias” have no proper place in metrology (because we can't know them).
- *NO!* “True value” (and its dependent terms) are readily defined.
- The whole of statistics is based on the idea of unknown population values, a concept logically isomorphic with “true value”.

Metrological false premise 6

- Only accredited laboratories can produce reliable results.
- **No!** Evidence from proficiency tests contradicts this idea.



Metrological false premise 6



Metrological false premise 6

