Setting standards in analytical science

Uncertainty arising from sampling

S Ellison (LGC Limited)
M Ramsey (University of Sussex)

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Introduction

- Does measurement uncertainty include sampling?
- How to estimate uncertainties from sampling
- Uncertainties from sampling in the food sector

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Measurement uncertainty

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ISO definition

"A parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand"

22.7 ± 4.8 g

The part of the result after the ±

Does measurement uncertainty include sampling?

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EURACHEM position

- If the measurand relates to a bulk material from which samples are taken for analysis, the uncertainty in the estimated value for the measurand must include the uncertainty arising from the sampling process
- If the result is reported on the sample 'as received' by the laboratory, only within-laboratory sub-sampling contributes to the uncertainty

Examples

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- Measuring and reporting the amount of pesticide in a laboratory sample of capsicum (green peppers)
  - Little or no sampling/subsampling
  - Sampling is not pat of the measurement process
- Reporting the average level of pesticide in the bulk container (consignment) from which the laboratory sample was taken
  - Sampling may greatly affect the reported result
  - Sampling uncertainty matters

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Estimating sampling uncertainty

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Different approaches to control of sampling

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- Gy: Well respected, based on management and control to eliminate sampling uncertainties
- Sampling uncertainties quantified using replication
  - Ramsey et al
  - Eurachem Guide
- Applying modelling approaches to sampling uncertainty
  - Minkkinen et al

Four empirical methods for estimating uncertainty

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Method #	Method description	Samplers (People)	Protocols	Component estimated			
				Sampling Precision	Sampling Bias	Anal. Precision	Anal. Bias
1	Duplicates	single	single	Yes	No	Yes	No[1]
2	Multiple protocols	single	multiple	between protocols		Yes	No [1]
3	CTS	multiple	single	between samplers		Yes	Yes [2]
4	SPT	multiple	multiple	between protocols +between samplers		Yes	Yes [2]

CTS = Collaborative Trial in Sampling , and SPT = Sampling Proficiency Test.

Simplest Empirical method is 'Duplicate Method

1 estimate analytical bias using CRM, 2 Analytical bias partially or completely included where multiple labs involved

Using the ‘duplicate method’
1) Separating sampling and analysis

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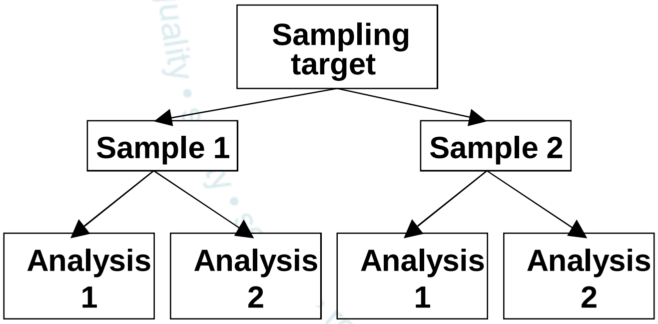

Sampling target:
Portion of material, at a particular time, that the sample is intended to represent.

Using the ‘duplicate method’
2) Replicating sampling

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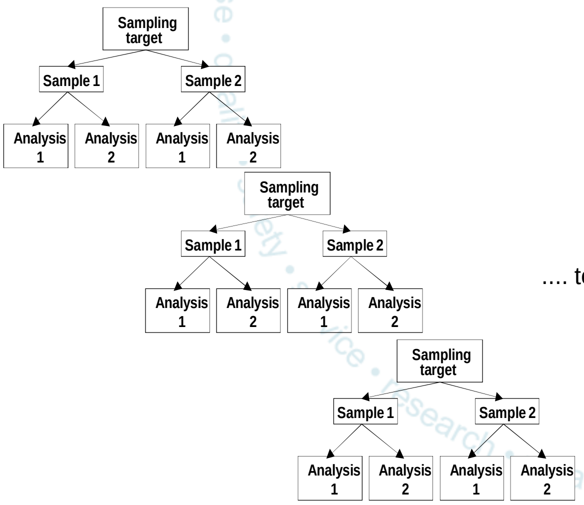
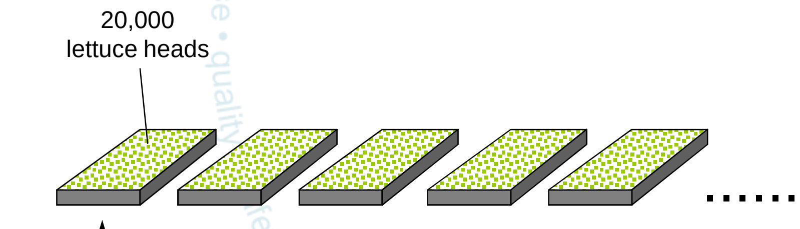


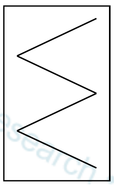
.... to at least 8 sampling targets

Statistical Analysis for the duplicate method

- Fully nested, balanced 2-way layout
- Analysis of variance gives sampling and analytical variance
  - each corresponding to a relevant standard uncertainty contribution
- Robust analysis of variance (RANOVA) suggested for outlier-contaminated data

Example: Nitrate in lettuce (Eurachem Guide p 35ff)





Sampling layout per bay:

- Every bay sampled
- Decision for each bay

Example 1: Duplicate method

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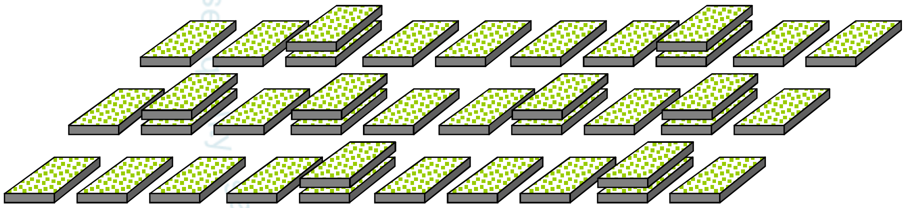
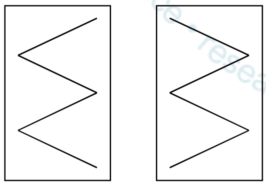


8 (or more) targets sampled in duplicate



Duplicate sampling arrangement

Example: Analysis

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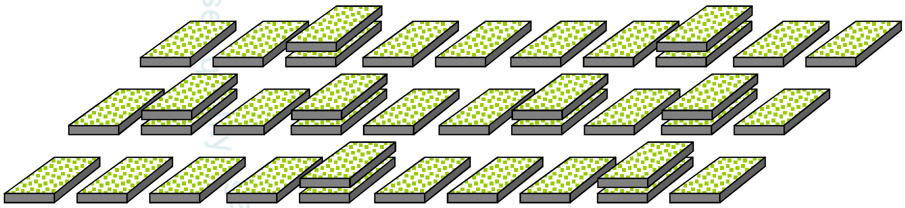

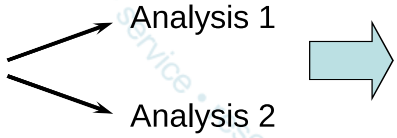

8 sampling targets

Sampled in duplicate

Each sample duplicate analysed in duplicate

Example: Results

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SAMPLE TARGET	S1A1	Uncertainty	x - U	x + U	Probabilistic Classification
A	3898	639	3259	4537	Poss Cont
B	3910	641	3269	4551	Poss Cont
C	5708	936	4772	6644	Cont
D	5028	825	4203	5853	Prob Cont
E	4640	761	3879	5401	Prob Cont
F	5182	850	4332	6032	Prob Cont
G	3028	497	2531	3525	Uncont.
H	3966	650	3316	4616	Poss Cont

Example 1: Results

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Robust ANOVA:

- s_{samp} = 319.05 mg kg^{-1}
- s_{anal} = 167.94 mg kg^{-1}
- $s_{meas} = \sqrt{(s_{samp}^2 + s_{anal}^2)}$ = 360.55 mg kg^{-1}

Classical ANOVA:

- s_{samp} = 518.2, s_{anal} = 148.2; s_{meas} = 538.9 mg kg^{-1}

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Sampling uncertainties in food analysis

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Review of sampling uncertainties in foods: Overview

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- Collate available data from literature
  - 23 sources identified
  - 30 product types
  - 59 product/analyte combinations
  - 13 products in retail environments; 17 factory/wholesale
- Apply duplicate method to increase data set on foods of interest
  - A further 16 product/analyte combinations
- Review sampling uncertainties for trends

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Results: Sampling/analytical ratios

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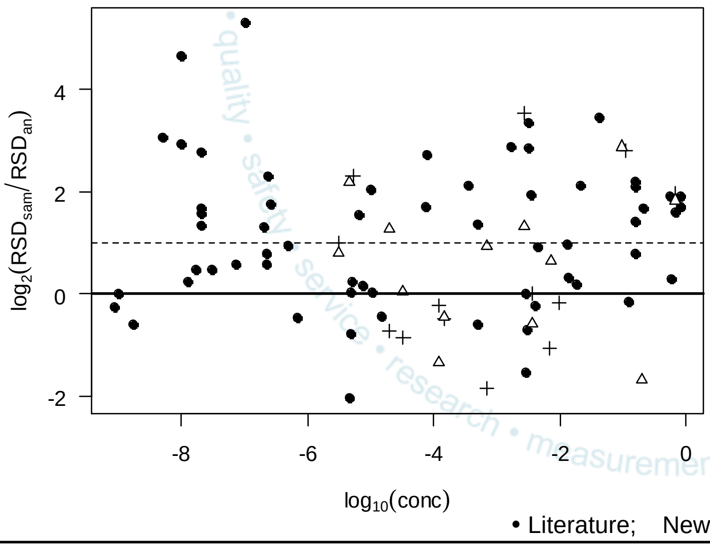

Most sampling uncertainties are larger than analytical precision

Some evidence of trend with analyte concentration

Trends with concentration i) Raw results

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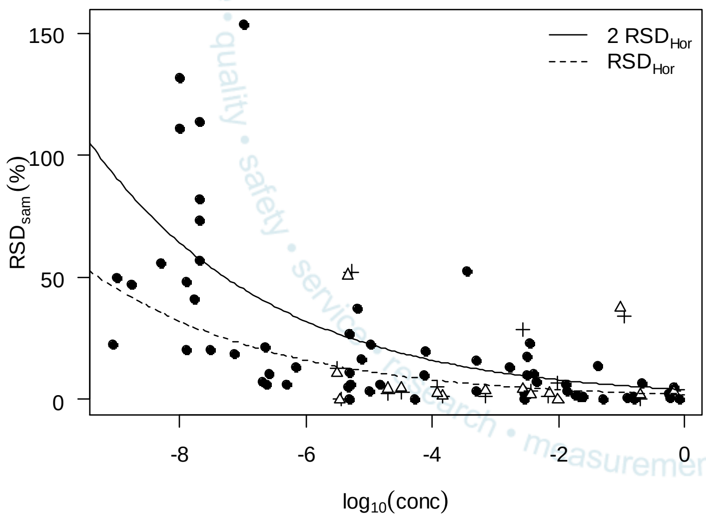

Sampling RSD increases with decreasing analyte concentration

Trends with concentration i) log-log relationship

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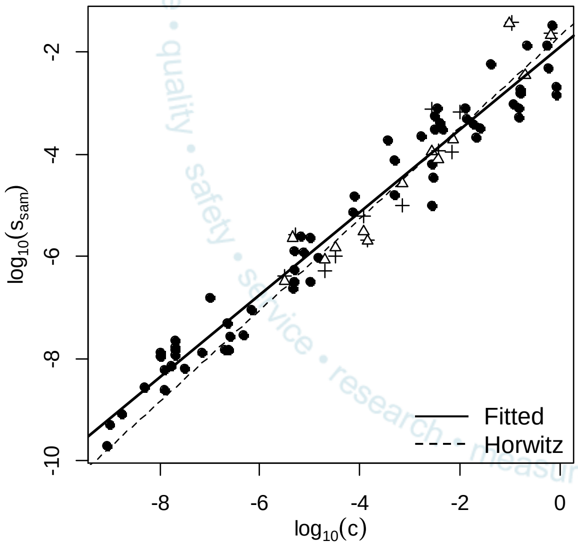

A Horwitz-like function describes sampling SD

The relationship is very approximate

Limitations

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- Literature surveys reflect interest in sampling
  - Possibly biased towards known problems
- Experimental work chosen to provide a range of examples
  - not a random sample of sampling
- Values differ from fitted line by about ±1 in $\log_{10}$:
  - Approximately one order of magnitude
- Sampling variation need not follow any particular distribution

Practical implementation

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- The duplicate method requires a minimum of 8 replicated sampling targets, or 16 sampling exercises
  - Economical only when many more increments are normally taken and measured separately
- Most useful when developing or comparing proposed sampling strategies in practice?

Conclusions

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- Primary sampling from the bulk contributes to the uncertainty when the measurand is defined as a property of the bulk material
- Relatively economical empirical approaches to estimating sampling uncertainty are available
- Sampling uncertainties are often considerably larger than analytical uncertainty
- Available data suggest that sampling standard deviation can be predicted to approximately an order of magnitude

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