Overview of Uncertainty from Sampling and the Eurachem UfS Guide (2019)

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Eurachem/Eurolab Workshop,
Uncertainty from sampling and analysis for accredited laboratories
November 2019, Berlin

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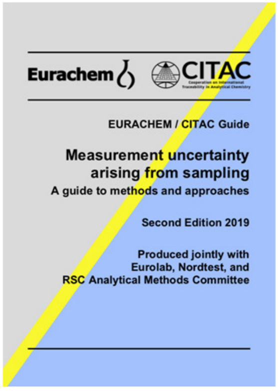

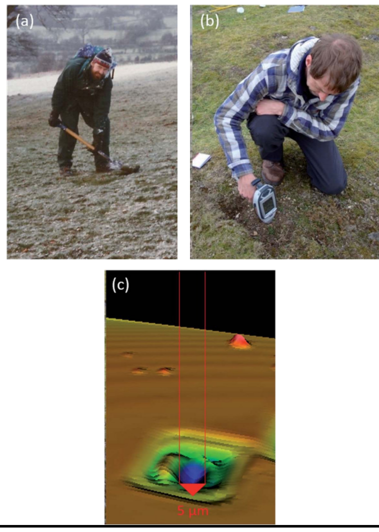

Overview

- Sampling as part of the measurement process
- Uncertainty (U) in measurement and sampling -
  - *key parameter of measurement (and sampling) quality*
  - *Brief overview of UfS estimation*
- Rationale for revision of UfS Guidance (2019)
- Focus on <u>New Aspects</u> to Guidance
  1. Uncertainty Factor – *explained in my later talk*
  2. Unbalanced experimental design to reduce the cost of estimating UfS - *in later talk (by Peter Rostron)*
  3. Application of UfS estimation to wider range of measurement types – e.g. *in situ*, passive and micro-scale measurements – *in other talks*
  4. UfS estimation using Sampling Proficiency Testing - *here*
- Conclusions

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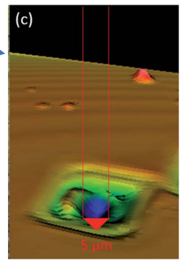
Sampling as part of the measurement process

- Sampling is really the first step in the measurement process (traditional sampling at the macro scale, e.g. soil)
- *In situ* measurement techniques – sampling integral
  - Place the sensor→ make measurement
    - taking a ‘beam’ sample at micro scale (e.g. mm or μm)
  - Uncertainty in sampling produces U in measurement value
- Physical sample preparation (in field or lab)
    - e.g. filter, acidify, dry, store, sieve, grind, split
  - is also part of the measurement process
  - and potentially important source of U
- Include both in validation and QC processes

hand-held portable X-ray Fluorescence (pXRF) on soil at 5 mm scale



Secondary Ion Mass Spectrometry (SIMS) on quartz, illustrating 5 μm beam scale

Analytical Methods Committee (2018) AMC Technical Brief No 84. Beam sampling: taking samples at the micro-scale, ***Analytical Methods*, 10, 1100-1102**

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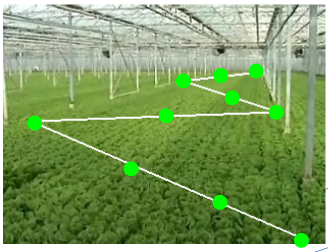
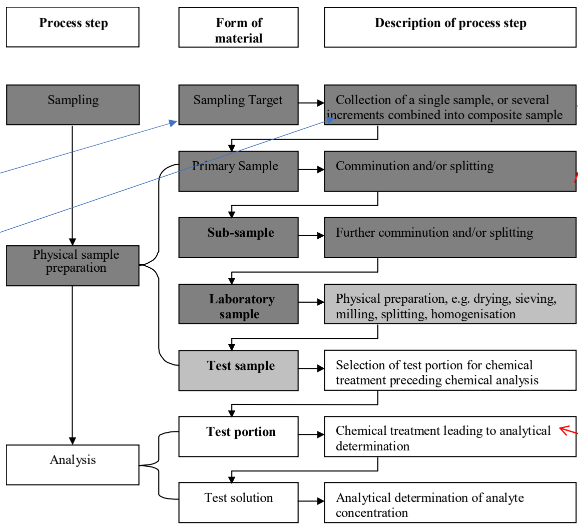
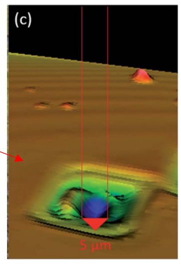
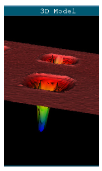
Sampling as part of the measurement process



x10







Primary sample
= Test portion mass from SIMS crater ~ 300-350 pg

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Sampling as part of the measurement process

If objective is to measure true value of analyte concentration (or measurand)
- in **sampling target** *(e.g. batch of food, area of soil, a crystal etc.)*
- Sampling is included in measurement process
- UfS part of measurement uncertainty (& method validation and QC)

If measurand (or true value) defined solely in terms of laboratory sample
- Primary sampling is not included

- Most <u>users</u> of analytical measurements assume x ± U apply to target
  - not just to lab sample

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Methods for estimating uncertainty of measurement *(including sampling)*

- What are the options?
  1. Empirical methods - 'Top down' approach
     - based on replicate measurements (within or between organisations)
     - *applicable to any system*
     - *Examples in the Guide – for food (A1, A4), soil (A2) and water(A3)*
  2. Modelling methods - 'Bottom up' approach
     - based on identifying, estimating and summing all of the components = 'Budget Modelling Approach' – *Example in Guide for top soil (A6)*
       - (Kurfurst *et al*, 2004, Accred Qual Assur., 9, 64-75)
     - sometimes Modelling using Sampling Theory (e.g. Gy's) to estimate components in particulate systems
       - (Minkkinen 2004, Chemometrics and Intelligent Lab. Systems, 74, 85-94)
       - *Example in Guide for animal feed (A5)*

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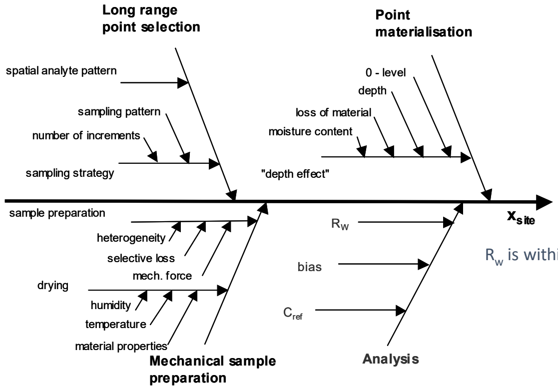
Budget Modelling Approach *to estimating U* - *Cause & effect diagram*



R_w is within-laboratory reproducibility

Example A6 for top soil in UfS Guide

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Budget Modelling Approach *to estimating U*

Summation of all individual components of uncertainty

-e.g. applied to concentration of Cd and P in field of arable top soils

$$\bar{x}_{site} = \bar{x}_{anal} \times f_{b-loc} \times f_{strat} \times f_{depth} \times f_{prep} \times f_{dry}$$

- $\bar{x}_{site}$ = measurement result
- $\bar{x}_{anal}$ = mean from the analysis of test samples
- $f_{\text{b-loc}}$ = correction factor for deviation "between locations"
- f_{strat} = correction factor for bias due to sampling strategy
- f_{depth} = correction factor for the "depth effect"
- f_{prep} = correction factor for errors during mechanical sample preparation
- f_{dry} = correction factor for deviation of moisture content

$$u_{site} = \sqrt{u_{anly}^2 + u_{b\text{-}loc}^2 + u_{strat}^2 + u_{depth}^2 + u_{prep}^2 + u_{dry}^2}$$

Explained by Ulrich Kurfürst in Example A6

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Modelling using Sampling Theory

Sampling theory of Gy defines 8 sampling errors

- includes 'fundamental sampling error' described by:-

$$\sigma_r^2 = Cd^3\left(\frac{1}{M_S} - \frac{1}{M_L}\right)$$

$\sigma_r = \frac{\sigma_a}{a_L}$ = Relative standard deviation of the fundamental sampling error = $u'_{sampling}$

σ_a= absolute standard deviation (in concentration units)

a_L = average concentration of the lot

d = characteristic particle size = 95 % upper limit of the size distribution

M_S = Sample size

M_L = Lot size

Explained by Pentti Minkkinen in Example A5 for animal feed

General relationship: **$s^2 \propto 1/m$** – useful in modifying UfS estimated by any method

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Empirical estimation of uncertainty: Statistical model

$$x = X_{true} + \varepsilon_{sampling} + \varepsilon_{analytical}$$

x = *measured* value of the analyte concentration in the sampling target

X_{true} = *true* value of the analyte concentration in the sampling target

$\varepsilon_{sampling} + \varepsilon_{analytical}$ = effects on measured concentration from sampling and analysis

Variance of measurement = $s^2_{meas} = s^2_{sampling} + s^2_{analytical}$

- includes between-organisational effects (e.g. sampling & analytical bias)

Standard uncertainty = $u_{meas} = s_{meas}$

Relative expanded uncertainty as % (for 95% confidence) = $U' = 100 \times 2s_{meas}/\bar{x}$

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Empirical methods for estimating uncertainty of measurement *(including sampling)*

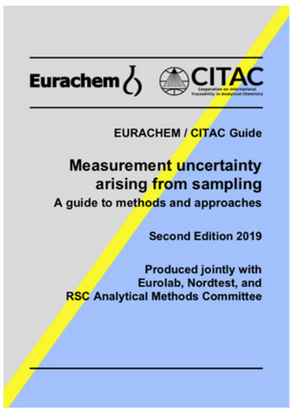
Method #	Method description	Samplers (persons)	Protocols	Component estimated		
				Sampling		Analytic
				Precision	Bias	Precision
1	Duplicates	Single	Single	Yes	No	Yes[3]
2	Protocols	Single	Multiple	Between protocols		Yes[3]
3	CTS	Multiple	Single	Between samplers		Yes
4	SPT	Multiple	Multiple	Between protocols +between samplers		Yes

- [1]Analytical bias information may be obtained by including certified reference materials in the analytical run (see Example A2, Appendix A).
- [2]Analytical bias is partially or completely included in collaborative exercises where multiple laboratories are involved.
- [3]In these approaches, precision is estimated under repeatability conditions

- Examples of Method #1 (*see later talk*) and Method #4 (using SPT) *discussed here*

Rationale for revision of UfS Guidance

- Second Edition of the Eurachem UfS Guide*
  - initiated to update, explain and integrate several recent research developments
  - whilst leaving most of the text unchanged
- Retains the same basic approach and structure as First Edition of 2007
  - based on concept that primary sampling as first part of measurement process
  - two main approaches to estimating UfS
- Six worked examples retained
  - demonstrate both approaches
  - across a range of application sectors, including food, animal feed, soil and water.
  - two of the examples partially updated to illustrate some of research developments
- Four main aspects of new developments included in Second Edition:-



*M H Ramsey, S L R Ellison and P Rostron (eds.) Eurachem/EUROLAB/ CITAC/Nordtest/AMC Guide: *Measurement uncertainty arising from sampling: a guide to methods and approaches.* Second Edition, Eurachem (2019). ISBN (978-0-948926-35-8). Available from http://www.eurachem.org

1. Using Uncertainty Factor to express MU and UfS

- Uncertainty Factor (^{F}U) is an alternative way to express measurement uncertainty.
- Upper and lower confidence limits (UCL & LCL) of a measurement value expressed by:-
  - multiplying and dividing the measurement value by the uncertainty factor
  - e.g. For measurement value of 5 mg/kg,

    $^{F}U = 2.5$ UCL = 5 * 2.5 = 12.5 mg/kg, LCL = 5/2.5 = 2 mg/kg

  Contrasts against traditional approach of adding and subtracting the uncertainty.
  - e.g. For measurement value of 5 mg/kg.

    $U = 2.5$ mg/kg UCL = 5 + 2.5 = 7.5 mg/kg, LCL = 5 – 2.5 = 2.5 mg/kg

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New Aspect 1. Using Uncertainty Factor to express MU and UfS

- Uncertainty Factor (^{F}U) is approach more accurate when:-
  - relative expanded uncertainty value is large (e.g. >20%),
  - frequency distribution of uncertainty is approximately log-normal, rather than normal.
- Both conditions often apply to measurement uncertainty that arises from sampling process,
  - particularly when spatial distribution of analyte in test material is substantially heterogeneous.
- Also for some purely analytical systems (e.g. GMO in soya, with $u' = 70\%$)
- Guide also explains how measurement uncertainty can be calculated
  - by adding the component arising from sampling, expressed as an uncertainty factor (^{F}U)
  - with that arising from chemical analysis, expressed as relative uncertainty (U')
- *More details of these issues in my later talk*

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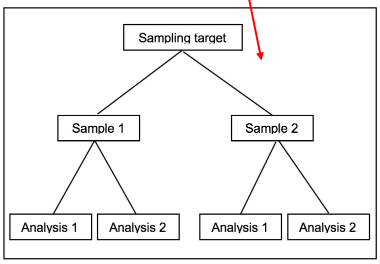
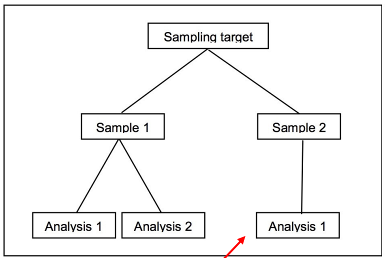
New Aspect 2. Unbalanced design to reduce cost of estimating UfS

- First edition used 'duplicate method' with a balanced experimental design for estimation of:-
  - measurement uncertainty as a whole
  - and its two components in sampling and analytical steps
  - using balanced design (analytical duplicates on both of the two sample duplicates)





- Second edition stresses the advantage of using unbalanced design,
  - analytical dreduces the extra cost uplicate on only one of the two sample duplicates.
  - of estimating the uncertainty by 33%.
  - *details in later talk by Peter Rostron*

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New Aspect 4. UfS estimation using Sampling Proficiency Testing

- First Edition of UfS Guide this approach was discussed in theory
- Second Edition now refers to the first practical example
- Multiple samplers each apply whatever sampling protocol they consider appropriate
  - to achieve the same stated objective for the same sampling target
- Using a balanced design across all of the different samplers (next slide)
- Then possible to include 'between-sampler' bias in estimate of UfS
  - in addition to the components that were previously included
- General principles of SPTs*
- First practical SPT used to estimate UfS**
  - concerned measurement of moisture content of 20 ton batch of fresh butter

-***Proficiency testing of sampling.** Technical Brief 78, July 2017, Anal. Methods, 2017, 9, 4110, DOI: 10.1039/c7ay90092a
-https://pubs.rsc.org/en/content/articlehtml/2017/ay/c7ay90092a
**M H Ramsey. B Geelhoed, A P Damant, R Wood (2011) Improved evaluation of measurement uncertainty from sampling by inclusion of between-sampler bias using sampling proficiency testing. Analyst, 136 (7), 1313 – 1321. DOI:10.1039/C0AN00705F

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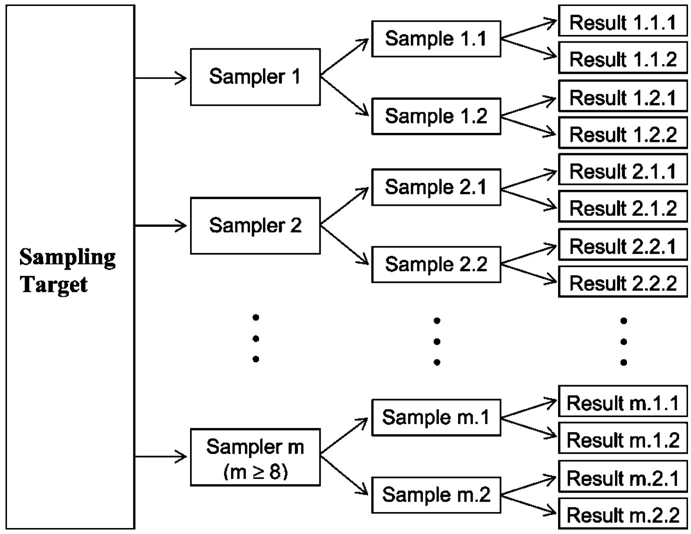
Experimental Design of SPTs



- Each sampler takes two samples,
  - both analysed twice
  - In balanced design
- Allows effects of analysis to be removed from those of sampling
- Multiple targets measured
  - in different rounds of the SPT

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σ_{pt}

Scoring an SPT – *in general*

$$z = (x - x_{pt}) / \sigma_{pt}$$

x = submitted result

e.g. participants estimated mean concentration of the sampling target

x_{pt} is assigned value

- independent of the result, either…
  - by expert/prior measurement
  - by spiking
  - by consensus

σ_{pt} is fitness for purpose (FFP) criterion

- independent of the result, either…
  - from external FFP requirement, or
  - from internal information (e.g. $s_{within\text{-}participant}$)

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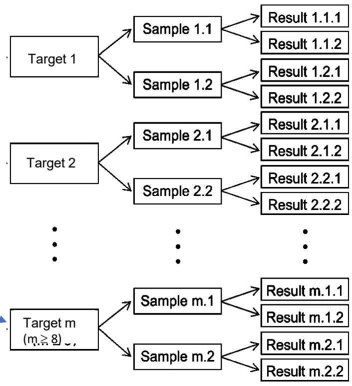
Uncertainty estimation from SPT

- Use ANOVA to separate the component variances (s^2)

$$s^2_{total} = s^2_{between-sampler} + s^2_{within-sampler} + s^2_{analytical}$$

- Use s^2_{total} as estimate of the measurement uncertainty
- Extra component is between-sampler effect
  - includes sampling bias – between-samplers
    - comes out as random effect in this model
  - not estimated by the **'Duplicate method'** usually used
    - by <u>single</u> sampler on 'm' different targets (m ≥ 8)
    - using balanced design
- UfS from Duplicate Method – for single sampler
  - estimated for butter using balanced design on single sampler
  - averaged across all samplers



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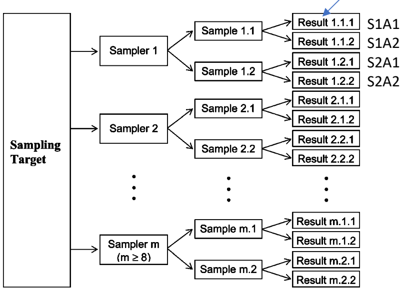
SPT on % Moisture in Fresh Butter

- Target: 20 tons of fresh butter in boxes – 6-fold composite sample
- Standard experimental design of SPT
- 9 samplers (A – I) operating independently
- % Moisture determined gravimetrically – by centralized analysis
  - Hence low analytical uncertainty (U' = 0.35%)



Sampler #	S1A1	S1A2	S2A1	S2A2
A	15.4741	15.4155	15.4972	15.4796
B	15.3655	15.3257	15.3653	15.3373
C	15.4417	15.4069	15.4552	15.4518
D	15.4161	15.4134	15.4486	15.4143
E	15.4085	15.3675	15.4392	15.406
F	15.4148	15.3876	15.4176	15.3473
G	15.4959	15.4757	15.4853	15.5185
H	15.3673	15.3732	15.372	15.3427
I	15.3214	15.2779	15.3424	15.3721

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Z- scores for SPT on Moisture in Fresh Butter

- z- scores calculated for both measurements (m.1.1 & m.1.2)
  - for two samples (m.1 and m.2) taken by each sampler (m)

Sampler	First z-score m.1.1	Second z-score m.1.2	Third z-score m.2.1	Fourth z-score m.2.2	Rescaled sum of z-scores = $\Sigma z/\sqrt{n}$ = $\Sigma z/\sqrt{4}$
A	1.36	0.18	1.83	1.47	2.42
B	-0.83	-1.64	-0.84	-1.40	-2.35
C	0.71	0.00	0.98	0.91	1.30
D	0.19	0.14	0.85	0.15	0.66
E	0.04	-0.79	0.66	-0.01	-0.06
F	0.16	-0.39	0.22	-1.20	-0.60
G	1.80	1.39	1.59	**2.26**	**3.52**
H	-0.80	-0.68	-0.70	-1.29	-1.73
I	-1.72	**-2.60**	-1.30	-0.70	**-3.16**

- Two samplers had potentially non-proficient RSz-scores* (> 3)
- Samplers; I (z = -3.2) & G (z = +3.5) – in opposite directions
- Video evidence suggests might be related to angle of sampling device

*AMC, Proficiency testing of analytical laboratories: organization and statistical assessment, Analyst, 1992, 117, 97–117.

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Estimate of Uncertainty using SPT - including Between-Sampler Bias

- Example using SPT for moisture in butter

ANOVA: U' as % on concentration of moisture in butter

≈ Duplicate Method (single sampler) gives **U' = 0.39 %**

SPT (multiple samplers, n=9) **gives U' = 0.87%**

- U′ larger* x 2.2 **- includes bias between-samplers**

Remove two samplers with potentially non-proficient z-scores (RSz > 3)

Samplers; I (z = -3.2) & G (z = +3.5)

SPT (n=7) gives **U' = 0.69%**

- ***U′*** **still larger x 1.8**
- **a more reliable estimate of Uncertainty**
- Ideally apply over multiple rounds of SPT, if targets comparable

Ramsey M.H. Geelhoed B, Damant, A.P., Wood, R. (2011) Improved evaluation of measurement uncertainty from sampling by inclusion of between-sampler bias using sampling proficiency testing. Analyst, 136 (7), 1313 – 1321. DOI:10.1039/C0AN00705F.

*Whether U′ values are significantly different – talk by Peter Rostron in 'Methods' Session

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Example of SPT using *in situ* measurements
NPL's Gas Measurement PT scheme

- Measurement of combustion gases
- From stack simulator facility at NPL (for sampling component)
  - and directly from cylinders (for analytical component)
- Concentrations and conditions are typical of plant
  - falling under Industrial Emissions Directive (IED)

Test	**NOx (ppm)**	**VOC (ppm)**	**SO_2 (ppm)**	**CO (ppm)**	**O_2 (%)**	**H_2O (%)**
Max Range	270	10	200	100	17	20

http://www.stack-pt-schemes.net/?page=stack_gases

- Results from 16 rounds published*
- (S)PT score used in accreditation
- UfS not yet estimates
- Combination of sampling and *in situ* analytical steps (i.e. measurement)
  - Better described as **Measurement Proficiency Test (MPT)** ?

*MD. Coleman et al, State of UK emissions monitoring of stacks and flues: an evaluation of proficiency testing data for SO2, NO and particulates, Accred Qual Assur (2013) 18:517–524, DOI 10.1007/s00769-013-1011-xhttp://www.npl.co.uk/measurement-services/environmental-monitoring/stack-proficiency-testing-scheme

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Review of published SPTs since 1995

Target Medium Synthetic target? (if in bold)		Analytes Central Lab? In situ test?	No. of Participants	No. of rounds	Ref	Comment
Soil	Top-Soil	Pb & Cu	9	1	[3]	First reported SPT realisation.
	Top-Soil	Pb & Cu	9	2	[6]	Improved performance in second round (s down 36% to 20%)
	Top-Soil	Ba	9	1	[7]	Spatial resolved SPT to locate 'hot spot'. Synthetic Target
Air	**Workplace**	Hydrocarbons Aromatic & Chlorinated	38	3	[8]	Not called an 'SPT', no z-scores. 3 sampling exercise each with sets of 4-8 runs. Has evidence for improved performance between rounds.
	Landfill-gas	*CH_4, CO_2, O_2*	9	1	[9]	Temporal variability monitored and corrected by reference borehole
	Stack gas	*Gases* & particulates	4	?	[10]	4 sampler at a time, use in-house-constructed emission simulation apparatus. Adapted homogeneity test for ISO 13528 compliance
	Stack gas	*Gases*	15	16	[11]	Run annually. 3 participants at a time, repeat over 4 to 8 days of testing. In-house constructed emission simulation rig allowing the testing of hot and wet test atmospheres. Homogeneity to EN15259.
Food (bulk)	Wheat	N, Mo, Pb	5	1	[12]	All participants used same protocol.
	Coffee	H_2O	8	1	[12]	All participants used same protocol.
	Lettuce 'in field'	NO_3^-	16	1	[13]	First example of virtual SPT, with participants from 16 different countries.
	Butter	H_2O	9	1	[5]	Results used to estimate U, including between-sampler bias.
	Apple Juice	Patulin	9	1	[14]	Not all SPT design criteria were met:- Limited access to the sampling target, ownership of the target, and this being the same as sampler's employer, limited independence of the samplers.
Water	Water-waste	COD, TOC, *pH,Temp*	16-20	3	[15]	*In situ* measurement of pH &Temp. Own labs used as well as central analysis. .

Wide range of sampling media, and analytes

Some targets spiked to derive assigned value

Some analyses done:
- *In situ*
- centrally by one lab

First example of virtual SPT,

Number of participants generally >8, up to 38

No. of Rounds
1 = feasibility assessment, multiple for ongoing SPT

Improved performance detected between rounds

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New #3. Application of UfS estimation to wider range of situations

- These include measurements made:
- (a) *in situ* (e.g. by field sensors without removing a sample)
- (b) on site (e.g. in a field laboratory on a removed sample)
  - Intermediate in complexity between *ex situ* and *in situ*
- (c) passive measurements of radioactive decay, and
- (d) at the microscopic scale (e.g. *In situ* PXRF in mm scale and SIMS at micron scale).
- *Discussed in later talk*

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Conclusions

- UfS needs to be included in estimates of Measurement Uncertainty – in most situations
- There are two main approaches to estimation UfS
  - empirical approach generally more flexible* than modelling approach
- Second edition of the Eurachem UfS Guide has several new aspects *(some discussed in later talks)*
- Use of Sampling Proficiency Testing data can help identify unsuspected* between-sampler bias

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Acknowledgements

Composition of UfS Working Group

Eurachem members

- Mike Ramsey (Chair)
- Steve Ellison (Secretary)
- Paolo de Zorzi (ISPRA, Italy)
- Pentti Minkkinen
- Eskil Sahlin (RISE. Sweden)
- Alex Williams

EUROLAB members

- Irache Visiers (Applus)
- Rudiger Kaus (EUROLAB, DE)

CITAC. Members

- Ilya Kuselman (Israel)
- Jorge Eduardo S Sarkis (INER, Brazil)

Nordtest representative

- Bertil Magnusson (Sweden)

RSC AMC representatives

- Roger Wood
- Peter Rostron

Additional members of RSC/AMC Subcommittee:-

- Bob Barnes
- Mike Thompson

Funding from Analytical Methods Trust (AMT)

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