

Identifying the new challenges for Uncertainty from Sampling (UfS)

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Overview – 4 Main Challenges:-

1. Improving how UfS (& MU) is estimated
2. Applying UfS estimation to a wider range of materials/situations
3. Improving the take-up of UfS estimation (as part of MU estimation)
4. Recognising the benefits of knowing UfS within MU (e.g. for VaMPIS)
+ A few other challenges



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1 Improving how UfS (& MU) is estimated

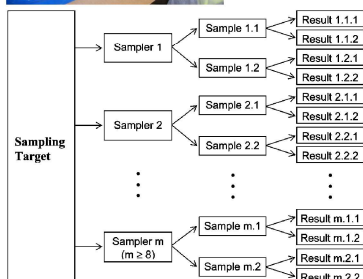
1a. Systematic effects (e.g. bias) from both analysis, and sampling (where possible)

- **Analytical bias** can be included in MU - approaches available (e.g. UfS Guide, Section 6.4, p 50)
- **Between-sampler bias** can be included in UfS (&MU) using measurement from CTS or SPT
 - One of the 4 approaches for empirical estimation of UfS (& MU), (Table 5, UfS Guide, 2019) :-

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

1b Estimate Uncertainty using Collaborative Trial in Sampling (CTS) including Between-Sampler Bias

- e.g. CTS for moisture in butter using single sampling procedure*



ANOVA: U' as % on concentration of moisture in butter (20 tons)

≈ Duplicate Method (Single Sampler) gives $U' = 0.39\%$

CTS (Multiple Samplers, n=9) gives $U' = 0.87\%$

- U' larger* x 2.2 – as includes bias between-samplers

Remove two samplers with potentially non-proficient SPT** z-scores (RSz > 3) (n=7) gives $U' = 0.69\%$

- U' still larger x 1.8

- a more reliable estimate of Measurement Uncertainty

- Hence more robust validation using VaMPIS – previous talk by Peter Rostron

- CTS more expensive than Duplicate Method, but sometimes justified

- high consequence cost of misclassification (e.g. gold mine)

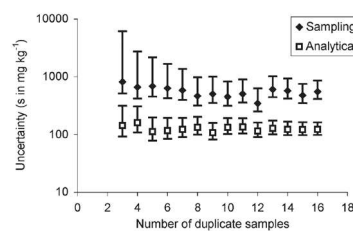
*Ramsey M. H., Rostron P. D. Collaborative Trial in Sampling for Validation of Measurement Procedures that Include Sampling. ACQUAL (Submitted, 2026)

**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.

1 Improving how UfS (& MU) is estimated

1b. Report Confidence Interval (CI) of UfS estimates reported, if required

- CI for both classical and robust estimates of UfS ($U_{f_{\text{analysis}}}$ & MU) can be calculated
 - e.g. in RANOVA3* (and RANOVA4)
- CI gets smaller with increasing n (more rapidly for UfS**)



Estimates of uncertainty produced by sampling (s_{samp}) and analysis (s_{ana}) of glasshouse-grown lettuce for nitrate (mg kg^{-1})**

*Rostron P.D., Fearn T., and Ramsey M.H. (2020) Confidence intervals for robust estimates of measurement uncertainty. Accreditation and Quality Assurance: 25, 107-119. <https://doi.org/10.1007/s00769-019-01417-4>

**Lyn, J.A., Ramsey, M.H., Coad, S., Damant, A.P., Wood, R. and Boon K.A. (2007) The duplicate method of uncertainty estimation: are eight targets enough? Analyst 132, 1147-1152 <https://doi.org/10.1039/B702691A>

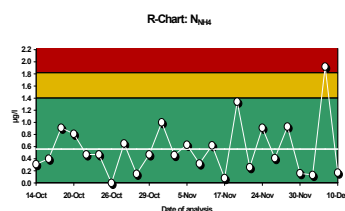
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1 Improving how UfS (& MU) is estimated

1c. Ongoing QC to monitor possible changes in UfS & MU after validation

Use **Integrated Measurement Quality Control (IMQC)**

- which includes both sampling and analysis (VaMPIS, Section 3)



Example of an R-chart for quality control of sampling (UfS Guide, p 30. For the construction of this R-chart see the Nordtest Guide*.)

- See whether the conditions present at validation are still present
- See whether initial estimates of U are still applicable
- Especially where subsequent targets very different (e.g. contaminated land)
- Perhaps add in separate estimate of heterogeneity for each site?
 - based on site history/land use – see later slide

*Magnusson B, Naykki T, Hovind H, Krysell M (2003) Handbook for Calculation of Measurement Uncertainty. NORDTEST report TR 537 (project 1589-02). Can be obtained from www.nordicinnovation.net/nordtest.cfm under link Rapporteur.

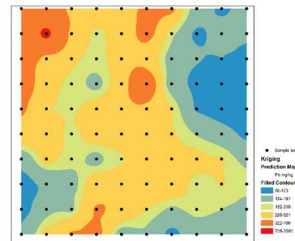
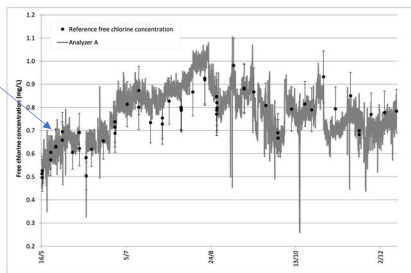
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2 Applying UfS estimation to a wider range of:-

2a. Different materials

- a. with spatial analyte heterogeneity*
- b. and/or temporal variability (e.g. Cl₂ in drinking water at treatment plant**)

Free chlorine concentration



Transcutaneous Bilirubinometer (TcB) – jaundice ?

2b. Application sectors

- a. e.g. environmental, food and feed, industrial processes, medical***

*Bettencourt da Silva, R., Argyraki, A., Borges, C., Ramsey, M.H. (2022) Spatial modelling of concentration in topsoil using random and systematic uncertainty components. Analytical Letters, 55, 2022, 14, <https://doi.org/10.1080/00032719.2022.2050383>
 **Guigues N, Raveau S., Major J, Canteau G., Béatrice Lalere B. (2025) Comparing EN 17075 and VaMPIS approaches for in situ continuous monitoring of free chlorine in drinking water. IMEKO TCS, TC11 and TC24 Conference <https://doi.org/10.21014/tc24-2025.035>
 ***Ramsey M.H. (2020) Challenges for the estimation of uncertainty of measurements made in situ. Accreditation and Quality Assurance 26(4), 183-192. <https://doi.org/10.1007/s00769-020-01446-4>



2 Applying UfS estimation to a wider range of:-

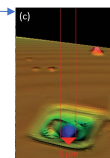
2c. Measurement types

a. ex situ

-transfer physical sample to the lab for analysis

- b. *in situ* - Taken *in situ* without disturbing or removing the test material
- Sampling indivisible part of measurement process, e.g.

- Soils - handheld portable (P)XRF for some metals (Example A2 in VaMPIS)
- Minerals – e.g. SIMS at micron scale
- Gases - many **sensors** – how most measurements are made!
 • e.g. Photoionisation detectors for VOCs, (e.g. benzene), IR for CH₄, CO₂
- Liquids - e.g. pH, UV-Vis for NO₃, TOC, H₂S



- Clinical - Transcutaneous Bilirubinometer (TcB) – jaundice ?

Passive *in situ* measurement of radioactive decay

- Case Study: ¹³⁷Cs in soil at Nuclear site (Dounreay) by γ -ray spec. with 100% coverage
- 1000 x larger sample mass than taken for *ex situ* analysis → lower UfS (U' 72% → 20%)
- (Different from 'Passive sampling' - commonly used for indoor air, water, sediments)

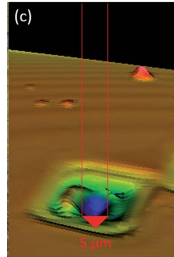
c. on site

- sample removed from original location, usually prepared/homogenised, measured close to original location
- intermediate in complexity between traditional *ex situ* measurements, and *in situ* measurements



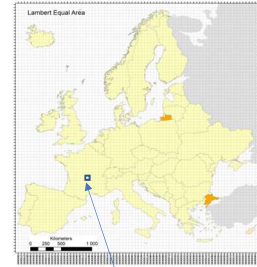
2^d Applying UfS estimation at different spatial scales

Sampling Target (at micro scale [μm])



e.g. Quartz Grain In candidate CRM for oxygen isotopes by SIMS

Sampling Target (at macro scale [km])



e.g. GEMAS survey of European soils
Each grid square 50 x 50 km

Sampling target	200 x 200 μm	50 x 50 m
Duplicate separation:	50 μm	<40m
Sample mass	~300 μg	2 kg

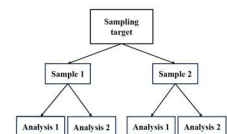
3rd Improving take-up of UfS (in MU) estimation

3a. Accreditation requirements (e.g. ISO/IEC 17025:2017)

3b. Reduced cost (e.g. using unbalanced and/or simplified experimental designs)

3c. Enhanced communication and collaboration between samplers and lab staff

Can be major impediment to take-up of VaMPIS



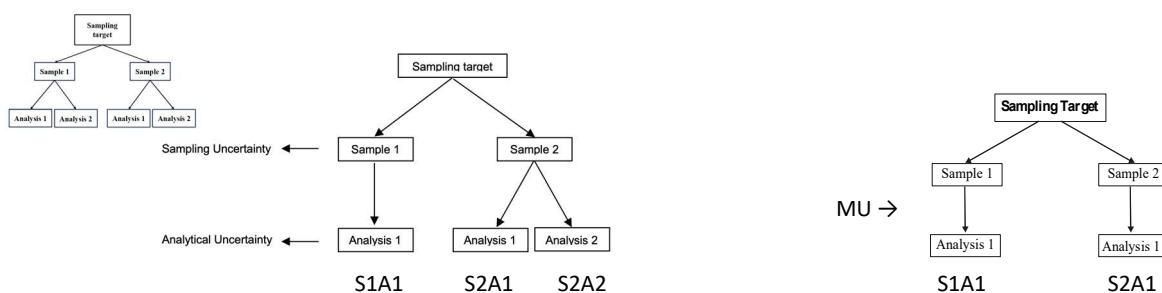
3^bImproving take-up of UfS (in MU) estimation

3a. Accreditation requirements (e.g. ISO/IEC 17025:2017)

Section 7.6.1 "Laboratories shall identify the contributions to measurement uncertainty. When evaluating measurement uncertainty all contributions that are of significance **including those arising from sampling**, shall be taken into account using appropriate methods of analysis".

- Challenges default assumption that $MU=U_{fA}$ for 'representative samples' taken using 'correct' procedure
- UfS may also be included in other standards (e.g. Medical sector in ISO 15189)

3^bReduced cost to encourage UfS estimation e.g. using unbalanced and/or simplified experimental designs



- **Unbalance design**
- Saves 33% of extra cost for UfS estimation
 - Allowed for in RANOVA3 software from AMC

- **Simplified balanced design**
- Saves 66% of extra cost, but..
- Only gives estimate of U_{meas}
- Needs external estimate of U_{anal}
- $U_{fS} = U_{samp}$ calculate by subtraction

3Improving take-up of UfS (in MU) estimation

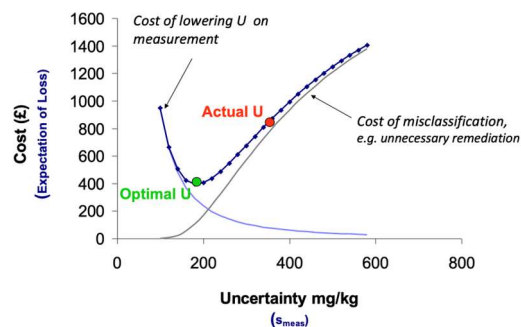
3c. Enhanced communication and collaboration between samplers and lab staff

- Major impediment to take-up of VaMPIS
- Integrated management of whole measurement process
- *Discussed in upcoming Breakout Session BS8 (and VaMPIS, Section 4)*

3d. Develop (e)training to help designers/samplers draw-up and implement experimental plans

4Recognising benefits of knowing UfS within MU

4a. Judging the fitness for purpose, and therefore more inclusive validation, of the whole measurement procedure that includes sampling (VaMPIS)



- a. Knowing MU (including MU) enable judgement of overall FFP – if not FFP then....
- b. Knowing UfS **contribution** to MU shows whether you need to **improve Sampling or Analysis** to achieve FFP
- a. Need more worked examples published (e.g. in different sectors)

4Recognising benefits of knowing UfS within MU

4b. More reliable compliance/conformity decisions,

- due to more realistic estimates of MU

Again, need more published case studies, with documented cost savings

- e.g. very high consequence cost (e.g. gold mine)

Other challenges: (1) Improve ways of Modifying UfS

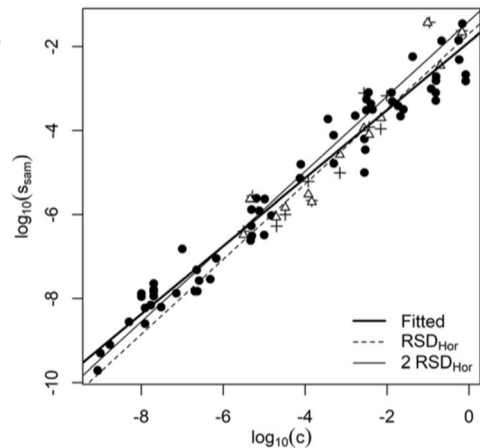
1. Improve ways of **Modifying UfS** in order to achieve Fitness-for-Purpose (FFP)
 - Why some systems behave in predictable ways ($s^2 \propto 1/m$), and others don't
 - Improve the modelling of UfS for such systems

Other challenges: (2) Variation of UfS within a sector

2. Compile **databases of UfS/UoM estimates across a whole sector** to see:

A. If there are typical values that could be used for prediction of UfS (e.g. by regulators)

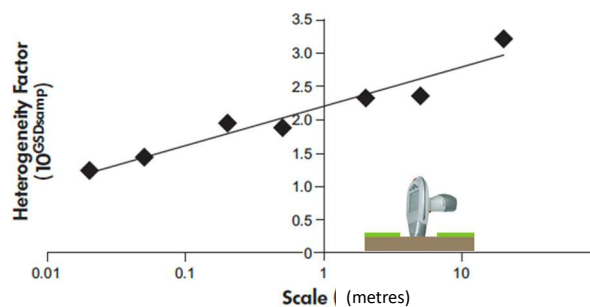
- As Ellison et al.(2017)*, did for **food sector**
- ~ 27 different food products (from field/store/factory/retail)
- ~75 different analytes
- Found Horwitz-like relationship
- provides estimate of UfS to within ~ an order of magnitude.



B. Get more evidence to test whether UfS increases as a function of concentration in other sectors

Other challenges: (3) Estimating site-specific *in situ* heterogeneity - as a component of UfS

- Using Duplicate Method with *in situ* devices (e.g. PXRF)
- Helpful when targets have different heterogeneity (e.g. contaminated land)
- Can be at any scale, or as a function of different spatial scales
 - with duplicates separated by different distances - e.g.*



Conclusions – 4 main Challenges

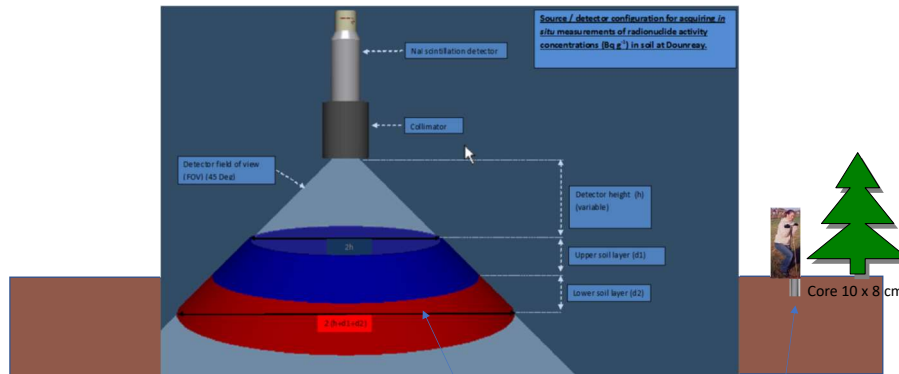


1. **Improving how UfS (& MU) is estimated** to include:-
 - a. systematic effects (e.g. bias) from both analysis, and sampling (where possible)
 - b. confidence interval of UfS estimates reported, if required
 - c. ongoing **IMQC** to monitor possible changes in UfS & MU after validation
2. **Applying UfS estimation to a wider range** of:-
 - a. different materials (with spatial analyte heterogeneity and/or temporal variability)
 - b. application sectors (e.g. environmental, food and feed, industrial processes, medical)
 - c. measurement types (e.g. *ex situ*, *in situ* [+ sensors], and on site)
3. **Improving the take-up of UfS (as part of MU) estimation** using:-
 - a. Accreditation requirements (e.g. ISO 17025)
 - b. Reduced cost (e.g. using unbalanced and/or simplified experimental designs)
 - c. Enhanced communication and collaboration between samplers and lab staff
 - d. Develop (e)training to help designers/samplers draw-up and implement experimental plans
4. **Recognising the benefits of knowing UfS within MU** in terms of:-
 - a. Judging the fitness for purpose, and therefore more inclusive validation, of the whole measurement procedure that includes sampling (VaMPIS)
 - b. More reliable compliance/conformity decisions, due to more realistic estimates of MU

Conclusions – other challenges

1. Improve ways of **Modifying UfS (to achieve FFP)**
2. Compile databases of **UfS/UoM estimates as function of concentration across a whole sector** - look for underlying pattern (~ Horwitz function)
3. Investigate benefits of **estimating site-specific *in situ* heterogeneity**, as a component of UfS

²²⁶Rn *In situ* measurements by γ -ray spectrometry



- *In situ* NaI detector responds to γ -rays (e.g. from decay of ¹³⁷Cs)
- Mass of soil 'sample' 200 -1000 kg
- ~1000 larger mass than physically extracted (e.g. ~ 0.5 kg)
 - for *ex situ* measurement by γ -ray spec.
- Hence lower UFS - U' reduced from 72% (*ex situ*) to 10% (*in situ*)

²²⁶Rn UFS estimation for On site measurements

- 'On site' measurements - when a sample taken from original location, usually prepared and homogenised, measured close to its original location.
- Situation is intermediate in complexity between traditional *ex situ* measurements, and *in situ* measurements

Example: Determination of total petrol hydrocarbons (TPH) in stockpiled soil*

- *ex situ* measurement made by on-site method
 - SiteLAB_UVF 3100 fluorescence spectrometer
- compared against those made in remote laboratory (GC-FID, with more QC)
- Duplicate method applied to both methods in usual way (+CRMs for bias)
 - on site [TPH] 3 x higher than off site measurement, maybe due to:-
 - loss of volatile TPH in samples taken off site
 - differences between the definitions of measurand for the two TPH analytical methods

