Sampling Aspects of BS10175:2010

The central role of uncertainty to judge fitness-for-purpose of SI

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11.25-11.40 (15 min)
Overview

• Traditional view of Sampling & Analysis - *separately*
• Benefits of integrated view of measurement process
• What is Uncertainty of Measurement (U)?
• Benefits of knowing U on every measurement
  – e.g. judging Fitness For Purpose (FFP)
• Case studies – show cost savings
• What needs to go into BSI 10175
• Conclusions
Traditional view of sampling & analysis

**Sampling:** – assume representative if you stick to the protocol

- 3.12 sampling
  
  *methods and techniques used to obtain a representative sample of the material under investigation*

- Estimate the uncertainty to see how representative sampling was

**Analysis:** assume measurements ≈ true values if accredited

- Ignore the fact that all measurements are wrong
  
  - to some extent

- measurements all have uncertainty
What is Uncertainty of Measurement?

3.7 Measurement uncertainty

- parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurement.

- Misquoted, should be ‘attributed to the measurand’
  - = ‘quantity intended to be measured’ (JCGM 200, 2008)*.
  - ~ true value of contaminant concentration

- Older definition clearer:-
  - An estimate attached to a test result which characterises the range of values within which the true value is asserted to lie (ISO 3534-1: 3.25, 1993)

- Sampling uncertainty: The part of the total measurement uncertainty attributable to sampling. IUPAC (2005)

- Analytical uncertainty: The part of the total measurement uncertainty attributable to chemical analysis.

### Case Studies - 6 routine Site Investigations

<table>
<thead>
<tr>
<th>Site</th>
<th>Area (ha)</th>
<th>Main type of contamination</th>
<th>Suspected source</th>
<th>Site end-use</th>
<th>Sampling method</th>
<th>Primary contaminant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>Heavy metal</td>
<td>Tin mining</td>
<td>Housing</td>
<td>Trial pits</td>
<td>Arsenic</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>Organic</td>
<td>Infill waste from gas works</td>
<td>Recreational land</td>
<td>Trial pits</td>
<td>Indeno(123) pyrene</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>Heavy metal</td>
<td>Infill after WWII bombing</td>
<td>Garden and allotment</td>
<td>Window sampling</td>
<td>Lead</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>Organic</td>
<td>Gas works</td>
<td>Hazard assessment</td>
<td>Trial pits</td>
<td>Total PAH</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>Heavy metal</td>
<td>Railway sidings and colliery spoil</td>
<td>Nature reserve</td>
<td>Trial pits</td>
<td>Arsenic</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>Heavy metal</td>
<td>Ex-firing range</td>
<td>Housing</td>
<td>Hand auger</td>
<td>Lead</td>
</tr>
</tbody>
</table>

Wide range of different:  
- sites (size, history & value),  
- contaminants, sampling methods


Estimation of uncertainty in a routine site investigation

Site 4 - Gas Works, East London

<table>
<thead>
<tr>
<th>Site</th>
<th>Area (ha)</th>
<th>Main type of contamination</th>
<th>Suspected source</th>
<th>Site end-use</th>
<th>Sampling method</th>
<th>Primary contaminant</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>12</td>
<td>Organic</td>
<td>Gas works</td>
<td>Hazard assessment</td>
<td>Trial pits</td>
<td>Total PAH</td>
</tr>
</tbody>
</table>
Estimating U

using the Duplicate Method

(BS10175:2010 Annex D)

Sampling

target

Sample 1

Sample 2

Analysis 1

Analysis 2

Analysis 1

Analysis 2

10% of Sampling targets in whole survey, $n \geq 8$

Sampling precision $s_{\text{Samp}}$

Analytical precision $s_{\text{Anal}}$

S1A1  S1A2  S2A1  S2A2

Eurachem Guide – better ref than older CLAIRE TB7
## Duplicate Results at Gasworks Site

<table>
<thead>
<tr>
<th></th>
<th>S1A1</th>
<th>S1A2</th>
<th>S2A1</th>
<th>S2A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.4</td>
<td>6.5</td>
<td>13.6</td>
<td>14.2</td>
</tr>
<tr>
<td>2</td>
<td>52.3</td>
<td>55.2</td>
<td>70.2</td>
<td>79.4</td>
</tr>
<tr>
<td>3</td>
<td>99.0</td>
<td>96.5</td>
<td>36.1</td>
<td>59.6</td>
</tr>
<tr>
<td>4</td>
<td>8.1</td>
<td>6.0</td>
<td>3.7</td>
<td>31.6</td>
</tr>
<tr>
<td>5</td>
<td>247.4</td>
<td>368.4</td>
<td>133.7</td>
<td>146.3</td>
</tr>
<tr>
<td>6</td>
<td>148.8</td>
<td>109.3</td>
<td>187.9</td>
<td>233.2</td>
</tr>
<tr>
<td>7</td>
<td>50.1</td>
<td>85.5</td>
<td>112.2</td>
<td>42.6</td>
</tr>
<tr>
<td>8</td>
<td>15.2</td>
<td>33.9</td>
<td>17.6</td>
<td>18.5</td>
</tr>
</tbody>
</table>

### PAH (mean conc 76 mg/kg)

<table>
<thead>
<tr>
<th></th>
<th>Standard Uncertainty (1s) mg/kg</th>
<th>Relative Expanded Uncertainty (2s) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling (inc prep)</td>
<td>27</td>
<td>71%</td>
</tr>
<tr>
<td>Analysis</td>
<td>20</td>
<td>53%</td>
</tr>
<tr>
<td>Measurement</td>
<td>34</td>
<td>89%</td>
</tr>
</tbody>
</table>

Much higher than quoted by lab - MCERTS 30%(2s) Precision
# Estimates of Uncertainty in 6 Case studies

<table>
<thead>
<tr>
<th>Site number</th>
<th>Key contaminant</th>
<th>U’random (%)</th>
<th>U’mes (%)</th>
<th>% of measurement variance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sampling</td>
<td>Analysis</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Arsenic</td>
<td>63.7</td>
<td>66.7</td>
<td>85.6</td>
</tr>
<tr>
<td>2</td>
<td>Indeno(123-cd)pyrene</td>
<td>50.8</td>
<td>54.6</td>
<td>80.3</td>
</tr>
<tr>
<td>3</td>
<td>Lead</td>
<td>25.3</td>
<td>32.2</td>
<td>58.9</td>
</tr>
<tr>
<td>4</td>
<td>Total PAH</td>
<td>89.3</td>
<td>91.5</td>
<td>60.5</td>
</tr>
<tr>
<td>5</td>
<td>Arsenic</td>
<td>157.6</td>
<td>158.9</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Lead</td>
<td>75.1</td>
<td>77.8</td>
<td>86.6</td>
</tr>
</tbody>
</table>

U’ meas (including analytical bias) ranges from 32 – 159% (at 95% confidence)

Main source of U is in the sampling (60-90% of total U)

- is this level of U acceptable – are measurement fit-for-purpose?
Judging Fitness-For-Purpose (FFP) using OCLI method.

• Estimates the Fitness-for-purpose (FFP) of measurements overall,
  – corresponds to minimum cost (expectation of lost)
  – sub-divide to estimate FFP of analytical and sampling components separately.

• Considers
  – all costs of measurement,
  – potential cost of misclassification
    – e.g. end-use, unnecessary remediation, potential litigation.

• Details in Ramsey M.H., Taylor P. D. and Lee J.C. (2002) Optimized Contaminated Land Investigation (OCLI) at minimum overall cost to achieve fitness-for-purpose, Journal of Environmental Monitoring, 4, 5, 809 - 814
Acceptable level of Uncertainty?

Cost (£) (Expectation of Loss)

Uncertainty mg/kg

Cost of lowering $U$ on measurement

Cost of misclassification, e.g. unnecessary remediation

Actual $U$

Optimal $U$
Actual v Optimal U for Gasworks Site

- Actual U = 34 mg/kg (U% = 89%)
  - Exp. Loss £11,000 per location

- Optimal U = 11 mg/kg (U% = 30%)
  - Exp. Loss £1700 per location

Overall saving of £74,400 on whole development
Financial Saving from optimal U

Expectation of financial loss estimated for whole sites for 6 routine site investigations.

Cost are calculated at either: uncertainty actually found (clear bars), or optimal value (black bars)

Site 6 has largest potential saving of £160,000

Reduce sampling uncertainty by taking composite samples (e.g. BS10175:2001)
e.g. 9-fold composite (‘cluster’) reduces U from Sampling by factor of ~ \sqrt{9} = 3
What needs to go into BSI 10175?

• Integrated view of measurement process
  – Sampling + Analysis
• Importance of realising all measurements are uncertain
• Need to report U value for all measurements (S&A)
• Enables:-
  – judgement of whether measurements are FFP
    • by investigator, user & regulator
  – Shows how to make measurements FFP (e.g. comp. samples)
  – Probabilistic interpretation of the site (e.g. EA, 2009)

• So:- ‘Strongly recommend estimation of Uncertainty from sampling’ (Sections: 5.7.1 Decision 4)
Estimating Uncertainty – Annex D

- Applies to field sampling (Sec 7.8 as QC?) sample prep & anal (Sec 9.3)
- When to ‘Estimating sampling uncertainty using the duplicate method *might be* (is generally recommended but ?) particularly appropriate when’:
  a) the confidence and robustness required of decisions to be based on the information from the site investigation is high; - ALWAYS?
  b) an investigation involves a large number of sampling locations - NO – just need 8 duplicates – so a minimum of 8 samples (i.e >10% of locations) - DELETE
  c) the analytical results are close to the site assessment criteria; - if away from T – show higher U (lower cost) justified
  d) the ground is expected to be highly heterogeneous.
  Common on contaminated site - don’t know otherwise without duplicate samples!

Explain practicality & utility - saving money on development overall, - judging and demonstrating fitness-for-purpose (FFP) *(add to list)*

Accepted in European Guidance – with contaminated land example*

- better to cite than earlier CLAIRE TB7
- also give design needed to quantify the contribution from sample preparation (Appendix D)

What needs to go into BSI 10175?(2)

• Don’t just consider UfS as part of QC = pass/fail – give values of Uncertainty to user

• **Composite samples – Importance for reducing U.**
  – Currently not recommended (7.6.2.6 Composite sampling and Table 9),
  – however ‘cluster samples’ = closely spaced incremental samples(8.3.2) ‘may’ be taken (e.g. for trial pits) – to make samples ‘representative’.
  – composite sample in international terminology – just with increments taken over a smaller scale than envisaged for the not recommended ‘composite’ samples.

• Reasons for not taking composite samples (sec 7.6.2.6) - can all be refuted if U known:-
  a) difficulty of comparing resultant data with guideline concentrations that relate to spot samples;
     – just lower measurement uncertainty
  b) possibility of disguising isolated locations of high concentration by mixing with samples of lower concentration;
     – not a problem with small-scale composites (~ ‘cluster samples’ over <1m²) - **Are** suitable for undisturbed sam
  c) possibility of loss of volatile compounds during the compositing processes;
     – also applies to spot/grab samples – needs separate treatment
  d) difficulty of achieving an adequately mixed and representative sample;
     – no sample is entirely representative (has uncertainty) but composite samples are more representative if properly prepared
  e) difficulty in undertaking statistical analysis of composited data.
     – OK is uncertainty known (lower for composite sample – if sampling target properly defined (e.g. small area, or one trial pit)

• 4.2 Setting investigation objectives- need to make sure measurements ~ FFP – need Uncertainty values

• Approach also applicable to on site and *in situ* measurements (8.4 On-site testing)
  – make ref to EA (2009)* gives worked example

Conclusions

1. Clearer definitions of sampling, measurement uncertainty, sampling uncertainty (section 3)

2. Broader introduction to the importance of estimation and reporting of uncertainty, rather than assumption of ‘representative’ sampling (Sections 7.8 & 10.3)

3. ‘Strongly recommend estimation of U from sampling’ (Sections: 5.7.2 Decision 4)

4. Revised wording in Annex D – to explain broader applicability and usefulness of duplicate method, e.g. for judging fitness-for-purpose

   – cite Eurachem Guide, rather than CLAIRE TB7, in Annex D

5. Recommend taking composite samples (over small area = cluster sample) if sampling uncertainty needs to be reduced (Sections 7.6.2.6 & 8.3.2)

6. State U approach also applicable to on site and in situ measurements - making reference to EA (2009) - (8.4.1 On-site testing)
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    - for application to on site measurements