Proficiency Tests and Interlaboratory Studies for Good Quality FR Analysis

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FR Analysis: Holistic Approach

Sampling → Plan – Objectives - Programme → Assessment

Sampling → Chemical Analysis → Data Analysis

TOTAL QUALITY MANAGEMENT

Storage → Co-ordination → Documentation

Chemical Analysis → Co-ordination → Data Analysis

IVM Institute for Environmental Studies
If we collect bad data:

- E.g. in UK:
  >30,000 analytical labs
  220,000 laboratory analysts
  100,000,000 analytical measurements per year
  3 analytical measurements per sec

The cost
Total value of the UK analytical services sector has been estimated to be UK 8.2 billion Euro per year.
It has been estimated that 10-20% of results are not 'fit-for-purpose', which costs:

0.8-1.6 billion Euro per year
OSPAR

- OSPAR rejects data that doesn’t meet at least minimum QC requirements
- 40 MEuro spent on generating monitoring data
- 50% of data was rejected from database
- 20 MEuros worth of work and it cannot be used
QA/QC - Definitions

• **QA**: All actions carried out to plan the proper performance of the analytical task

• **QC**: All operational techniques and activities that are used to fulfill requirements for quality
QA/QC - Tools

• Workplan
• Guidelines
• Calibration, Blanks
• Reference Materials
• Quality Chart
• Interlaboratory Studies/Proficiency Tests
<table>
<thead>
<tr>
<th>Substance</th>
<th>Matrix</th>
<th>Trend type</th>
<th>Sensitivity</th>
<th>Co-factors</th>
<th>Precautions</th>
<th>Frequency</th>
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<td>Metals</td>
<td>Air</td>
<td>Time</td>
<td>%</td>
<td>Fat</td>
<td>Ship</td>
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<td>Dry w.</td>
<td>Glassware</td>
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<td>Length</td>
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<td>Weight</td>
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<td>Point-source</td>
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<td>Age</td>
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Matrix

- Biota: fish, shellfish, other?
- If fish, which type, which length?
- How can we catch them in a representative way?
- Do we need a boat? (costs!)
- Do we pool them or analyse individuals?
- Which part/organ do we analyse?
- How is the transport to the lab?
- Do we need ice/dry ice?
Precautions

• Safety of sampling methods (nets, electricity)
• Do we need a license?
• Are there ethical issues?
• Which materials can cause contamination?
• Pen/paper to record observations?
Target Compounds

- Do we have standards? (order, costs)
- Quality of standards?
- Do we have an instrument to analyse them?
- Can we prepare proper calibration curves?
Required Sensitivity

• What is the expected concentration?
• Is our instruments sensitive enough?
• Do we need a specific detector?
• How much sub-sample do I need?
• How much sample is needed to ensure the minimum size of the sub-sample?
Blanks: DecaBDE in Jelly Fish

GC-ECNI-MS

Comb Jellies 0.014 ng/g ww

Blank (60 fg)
Boxcorer
Sampling: Contamination

- Plastic bags
- Ship (oil, dirt, exhaust gasses)
- Knives
- Filters
- Glassware
- Cross contamination
- One species
Effect of Poor Clean up

**Insufficient clean up**

- Hexa-mono-ortho-PCBs

**Suitable clean up**

- PCB 138
- PCB 167
- PCB 156
- PCB 157

**Hexa-mono-ortho-PCBs**
Sediments: Sulphur
Co-factors

- Which co-factors are we going to analyse?
- What are the implications for sampling?
- Fat? Which fat? (triglycerides, total fat)?
- TOC – Which method?
- Which method do we need? Is that available?
- Is it validated?
- Is there a reference material?
Sensitivity

1978 – 0.1 mg/kg

1988 – 1 μg/kg

1998 – 1 ng/kg

2008 – 10 pg/kg

X1000
Validation

- **Accuracy** = Precision (In-house) and Trueness (External)
- **Precision**: repeatability, reproducibility (IRM - QC Chart)
- **Trueness**: participation in PT scheme and use of CRM
- **Linearity**: calibration curves (multi-level if not linear)
- **Detection Capability**: LOD and LOQ: signal-to-noise level, blanks
- **Robustness/Ruggedness**: sensitivity for interference, dependency of matrix, influence of technician, etc.
Accuracy

- Poor trueness
- Poor precision

- Poor trueness
- Good precision

- Good trueness
- Poor precision

- Good trueness
- Good precision
Precision

• **Repeatability**

  5 replicates of e.g. LRM analysed in one series at one day by one technician at one instrument

• **Reproducibility**

  5 replicates of e.g. LRM analysed in different series at different days by different technicians at different instruments
Ruggedness

The ability of a method to be relatively insensitive to minor changes in the procedure, to the quality of reagents or to the environment
### PCB 118 gehalte in IRM 406

**Gegevens over voorgaande periodes**
- Gem +3S: 552.8
- Gem +2S: 520.5
- Gem: 455.9
- Gem -2S: 391.4
- Gem -3S: 359.1
- N: 148
- N lognorm: 2
- Sdev: 32.3

**Gegevens over deze periode**
- Gem +3S: 534.2
- Gem +2S: 509.9
- Gem: 461.1
- Gem -2S: 412.3
- Gem -3S: 387.9
- N: 30
- Sdev: 24.4

**Gegevens over alle waarnemingen**
- Gem +3S: 545.3
- Gem +2S: 513.7
- Gem: 450.4
- Gem -2S: 397.2
- Gem -3S: 355.5
- N: 243
- N lognorm: 7
- Sdev: 31.6

**Na 30 waarnemingen:**

\[ N_{S} \text{ lognormale waarnemingen} = 0.75 \]

\[ N_{S} \text{ lognormale waarnemingen} = 1.48 \]

\[ S_{S} \text{ lognormale waarnemingen} = 13.2 \]

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**Referentie materiaal:** IRM 406; kabelas-lever
**Referentie waarde:** NA

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</table>

**Waarnemingen**

| Waarneming | 221 | 222 | 223 | 224 | 225 | 226 | 227 | 228 | 229 | 230 | 231 | 232 | 233 | 234 | 235 | 236 | 237 | 238 | 239 | 240 | 241 | 242 | 243 | 244 | 245 | 246 | 247 | 248 | 249 | 250 |
|------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Gehalte in µg/kg |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |

| Opmerking |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |

**Afbeking = X**

| conform |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |

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**IVM Institute for Environmental Studies**
External Quality Control

- Interlaboratory Studies/Proficiency Tests
- Certified Reference Materials (CRMs)
Interlaboratory Studies

- One-off Studies
- Stepwise-designed studies (Learning exercises)
- Proficiency tests

Advantage: blind tests

We need interlab studies for
- Comparability of data
- For trueness
- For accreditation purposes
Stepwise Designed Interlaboratory Studies:

- Real samples
- Uncleaned Extracts
- Clean Extracts
- Solutions

Advice in every round
Proficiency Tests

• Routine schemes
• Regular distribution of test materials (e.g. 1 or 2x per year)
• Direct report to participants
• Use of Z-scores
• Useful and mandatory for accreditation

Also: blind tests
Requirements: How Good should it be?

Assume we need to detect a 50% change in contaminant level, e.g. a decrease from 8 to 4:

Max. allowed CV should be ca. 25%, because in that case 8 may be 6 or 10 or in between, and 4 maybe 3 or 5 or in between:

\[ 6 < 8 < 10, \text{ and: } 3 < 4 < 5 \]
Z-scores

\[ z = \frac{(m - \mu)}{sd} \]

Example: \( \mu = 20 \), target st. dev. = 25% = 5,
- When result is 30 \( \Rightarrow \) Z-score = \( \frac{30 - 20}{5} = 2 \)
- When result is 40 \( \Rightarrow \) Z-score = \( \frac{40 - 20}{5} = 4 \)
$Z$-scores

$|Z| < 2$ Satisfactory performance

$2 < |Z| < 3$ Questionable performance

$|Z| > 3$ Unsatisfactory performance

$|Z| > 6$ frequently points to gross errors (mistakes with units during reporting, calculation or dilution errors, and so on).
The assigned value
Probability Density Function

\((\sum \text{OMFs})^2 = \text{Population Density Functions (PDFs) for BWE}\)

QOR076MS CB153
BLACK dots for histogram of All Data
BLUE area for Mode 1 PDF1
GREEN area for All Data
\[(\sum \text{OMFs})^2 = \text{Population Density Functions (PDFs) for BWE}\]

- **QOR053BT CB156**
- BLACK dots for histogram of All Data
- BLUE area for Mode 1 PDF
- GREEN area for All Data

**PMF1**
Different statistics

- PT providers use different statistics, e.g. with different treatment of outliers
- Outlier tests, e.g. : Grubb’s test
- Robust statistics: downweighting outliers
- Multivariate statistics
- Cofino statistics: probability density function
‘Kilt’-Plot

Kilt Plot (Overlap Matrix) – BWE QOR076MS CB153

Kilt Plot (Overlap Matrix) – BWE QOR053BT CB156
QUASIMEME: ‘Holistic Approach’

- Proficiency Tests
  - POPs, PAHs, Trace metals, Nutrients, Shellfish Toxins
- Learning Exercises
  - ‘New’ Contaminants
- Training Workshops
- Internet Exchange of Technical Questions
- Monitoring Long Term Performance Labs
## Results of Interlaboratory Studies for PCBs & OCPs

<table>
<thead>
<tr>
<th>Year No. Labs</th>
<th>Year</th>
<th>No. Labs</th>
<th>Matrix</th>
<th>R.S.D. PCB%</th>
<th>R.S.D. OCP%</th>
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<tr>
<td>2009-10</td>
<td>2006-10</td>
<td>37</td>
<td>Sed</td>
<td>42</td>
<td>117</td>
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<td>200002</td>
<td>1998</td>
<td>78</td>
<td>Sed</td>
<td>150</td>
<td>130</td>
</tr>
<tr>
<td>1997</td>
<td>48</td>
<td>47-150</td>
<td>25</td>
<td>39</td>
<td></td>
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<tr>
<td>2009-10</td>
<td>2006-08</td>
<td>37</td>
<td>Sed</td>
<td>83</td>
<td>70</td>
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<td>2000</td>
<td>55</td>
<td>45-140</td>
<td>65</td>
<td>90</td>
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<td>1993</td>
<td>Fish</td>
<td>19-180</td>
<td>7-160</td>
<td>41</td>
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<tr>
<td>1988</td>
<td>Fish</td>
<td>25</td>
<td>3-115</td>
<td>-</td>
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<tr>
<td>1988</td>
<td>Fish oil</td>
<td>39</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>
Trends in Performance of Laboratories

- **CBs % Labs with > 90% data | Z | <2**
- **CBs % Labs with > 75% data | Z | <2**
- **OCPs % Labs with > 90% data | Z | <2**
- **OCPs % Labs with > 75% data | Z | <2**

The chart shows the percentage of laboratories with satisfactory data across different years, with specific thresholds for data completeness.
DE8 Brominated Flame Retardants. - Continued

- BDE026
- QBC006SS

- BDE099
- QBC006SS

- BDE153
- QBC006SS

- BDE183
- QBC006SS

- BDE100
- QBC006SS

- BDE154
- QBC006SS
- BDE99 in standard solution
- BDE 47 in fish
- BDE47 in sediment
- BDE47 in sediment (II)
### Table 1: Summary Statistics for QUASIMEME Participants

<table>
<thead>
<tr>
<th>Matrix/terminand</th>
<th>Assigned Value</th>
<th>Units</th>
<th>Total NObs</th>
<th>Error%</th>
<th>Numerical Median</th>
<th>Robust Median</th>
<th>Between Lab CV%</th>
<th>Model Mean</th>
<th>Model s.d.</th>
<th>CV%</th>
<th>% data reported</th>
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<td>BC005MS</td>
<td>0.513</td>
<td>ug/kg</td>
<td>22.25</td>
<td>6</td>
<td>0.51</td>
<td>0.52</td>
<td>26.14</td>
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<td>0.02</td>
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<td>7.76</td>
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<td>1.15</td>
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