Proficiency Testing from the viewpoint of the provider

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Outline of Talk

- Brief introduction to operation of proficiency testing
- Critical issues for PT provider
  - Test materials (homogeneity)
  - Assigned value
  - Ensuring no method dependence in assigned value
  - Assigning target standard deviation ($\sigma$)
- Examples of problem areas – Sn, furan, HMF
- Conclusions
Organisation of FAPAS

Test Material Procurement and Homogeneity Testing

Distribution of Test Materials

Participants Analyse Test Materials

Participants Return Results

Statistical Analysis of Data

Distribution of a Confidential Report

Recommendations for Future Rounds
Importance of PT to participants

Ensures data are meaningful

Business critical

Linked to maintaining ISO 17025 accreditation

Contributes/enhances laboratory reputation
What participants want from proficiency testing

- Relevant test material with relevant analyte/concentration
- Confidence in homogeneity of test material
- Satisfactory z-score
  - Confidence in assigned value
  - Confidence in appropriateness of target standard deviation
Test materials

Not always easy to find naturally contaminated materials

Incurred tissues (veterinary drug residues)
  -time-consuming and expensive to prepare

Need to have confidence in analyte stability over 3-6 months

Need to be able to prepare in homogenised form

Need to demonstrate homogeneity
FAPAS® Homogeneity Data for Ochratoxin A in green coffee test material
Z-Scores

\[ z = \frac{(x - \hat{x})}{\sigma} \]

where \( x \) = reported value of analyte

\( \hat{x} \) = assigned value of analyte - ‘true’ concentration

\( \sigma \) = target value for standard deviation of values of \( x \)

\[ z = \begin{cases} 
\leq 2 & \text{‘Satisfactory’ 95\% well-behaved results} \\
2 < z < 3 & \text{‘Questionable’} \\
z \geq 3 & \text{‘Unsatisfactory’}
\end{cases} \]
## Example Table and Chart for Aflatoxin B$_1$

<table>
<thead>
<tr>
<th>Laboratory Number</th>
<th>Analyte</th>
<th>Assigned Value</th>
<th>AFB$_1$</th>
<th>Result</th>
<th>Recovery</th>
<th>Z-score</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>4.28</td>
<td>68.9</td>
<td>-0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>002</td>
<td>6.78</td>
<td>100</td>
<td>1.7</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>003</td>
<td>4.5</td>
<td>106</td>
<td>-0.4</td>
<td></td>
<td></td>
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<tr>
<td>004</td>
<td>5.0</td>
<td>86</td>
<td>0.0</td>
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<tr>
<td>005</td>
<td>5.56</td>
<td>88.6</td>
<td>0.5</td>
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<tr>
<td>006</td>
<td>3.2</td>
<td>80</td>
<td>-1.6</td>
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<tr>
<td>007</td>
<td>5.4</td>
<td>95.6</td>
<td>0.4</td>
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<tr>
<td>008</td>
<td>4.07</td>
<td>81.8</td>
<td>-0.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>009</td>
<td>1.0</td>
<td>96</td>
<td>-3.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>010</td>
<td>9.1</td>
<td>63.65</td>
<td>3.8</td>
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<tr>
<td>011</td>
<td>6.0</td>
<td>75</td>
<td>0.9</td>
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<tr>
<td>012</td>
<td>2.9</td>
<td>79.2</td>
<td>-1.9</td>
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<tr>
<td>013</td>
<td>8.20</td>
<td>101.62</td>
<td>2.9</td>
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<tr>
<td>014</td>
<td>7.09</td>
<td>103</td>
<td>1.9</td>
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<tr>
<td>015</td>
<td>3.82</td>
<td>113</td>
<td>-1.1</td>
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</tr>
</tbody>
</table>
The target standard deviation sets the limits of satisfactory performance in the PT.
### Influence of σ-values on z-scores

Total aflatoxins in peanut meal - mean 25.4 ppb

<table>
<thead>
<tr>
<th></th>
<th>Acceptable range ppb</th>
<th>Numbers of participants</th>
<th>% Satisfactory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horwitz</td>
<td>11.3 - 39.6</td>
<td>102</td>
<td>19</td>
</tr>
<tr>
<td>95% ±2 z-score</td>
<td>2.4 - 48.4</td>
<td>114</td>
<td>7</td>
</tr>
<tr>
<td>Best practice</td>
<td>15.8 - 35.1</td>
<td>86</td>
<td>35</td>
</tr>
</tbody>
</table>
True value and assigned value

- ‘True’ value is an ideal
- ‘Assigned value’ is the best estimate of the determinand
FAPAS® derives the assigned value from the most appropriate measure of central tendency:

- robust mean
- median
- mode
To satisfy PT Participants organisers MUST:-

- Be confident in assigned value
- Be confident that there is no method dependence in dataset
  - bump-hunting
‘Bump-hunting’ for the Mode(s)

Adaptive kernel density plot - C2

Bimodal Results – Poor Methodology?

Adaptive kernel density plot - chloride

Density

Analytical result
FAPAS 0738 – Tin in Tomato Paste

- Preparation
  - Spiked at 250 mg/kg
  - Homogeneity mean was 251 mg/kg

- Results from participants
  - Consensus of results was 204 mg/kg
  - Consensus was 20% lower than the spike
  - Homogeneity mean would have resulted in a z-score of 3.2
  - Using ICP-IDMS result was 247.8 mg/kg
0738 – Tin in Tomato Paste

Adaptive kernel density plot - all tin

Density

Analytical result
Issues with PT for tin analysis

- No correlation between methods used and the results received

- FAPAS protocol indicates that we should use the consensus value not the spike value

- Complaints from participants that obtained results that correlated with the spike value, but they received unsatisfactory z-scores
Analysis of furan in babyfood

- Furan – b.p. 31.4 °C
- Heat processing contaminant found in canned and jarred products e.g. baby food, soups, coffee and fruit juices.

Analysis:

- Static Headspace GC/MS or solid phase micro-extraction (SPME)-GC/MS
- Isotope dilution methodology with \(^{2}H_{4}\)-furan as internal standard
Z-Scores for Furan (59.6 µg/kg) in Baby Food
Z-Scores for Furan (59.6 µg/kg) in Baby Food

Adaptive kernel density plot - furan-valid

Labs using >60°C incubation temp
Hydroxymethylfurfural (HMF)

- HMF – quality indicator in honey (Regulatory limit <40 mg/kg)

Analysis:
  - Colorimetric method
  - HPLC – no clean-up
  - HPLC – SPE clean-up
Z-Scores for HMF by HPLC without SPE clean-up (21.8 mg/kg) in honey
Z-Scores for HMF (HPLC + SPE clean-up) (16.7 mg/kg) in Honey Test Material

(LC/MS method for HMF)
Concluding remarks

- Need to scrutinise PT datasets for any method dependence

- Cannot always assume majority of participants are always right !

- In controversial situations (eg Sn analysis) PT providers must persuade participants to adopt a critical approach
  - Scrutinise their own methodology
  - Adopt improvements
FAPAS website
For Further Information, Contact:

- Proficiency Testing Services for FAPAS®, FEPAS®, GeMMA and LEAP™

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