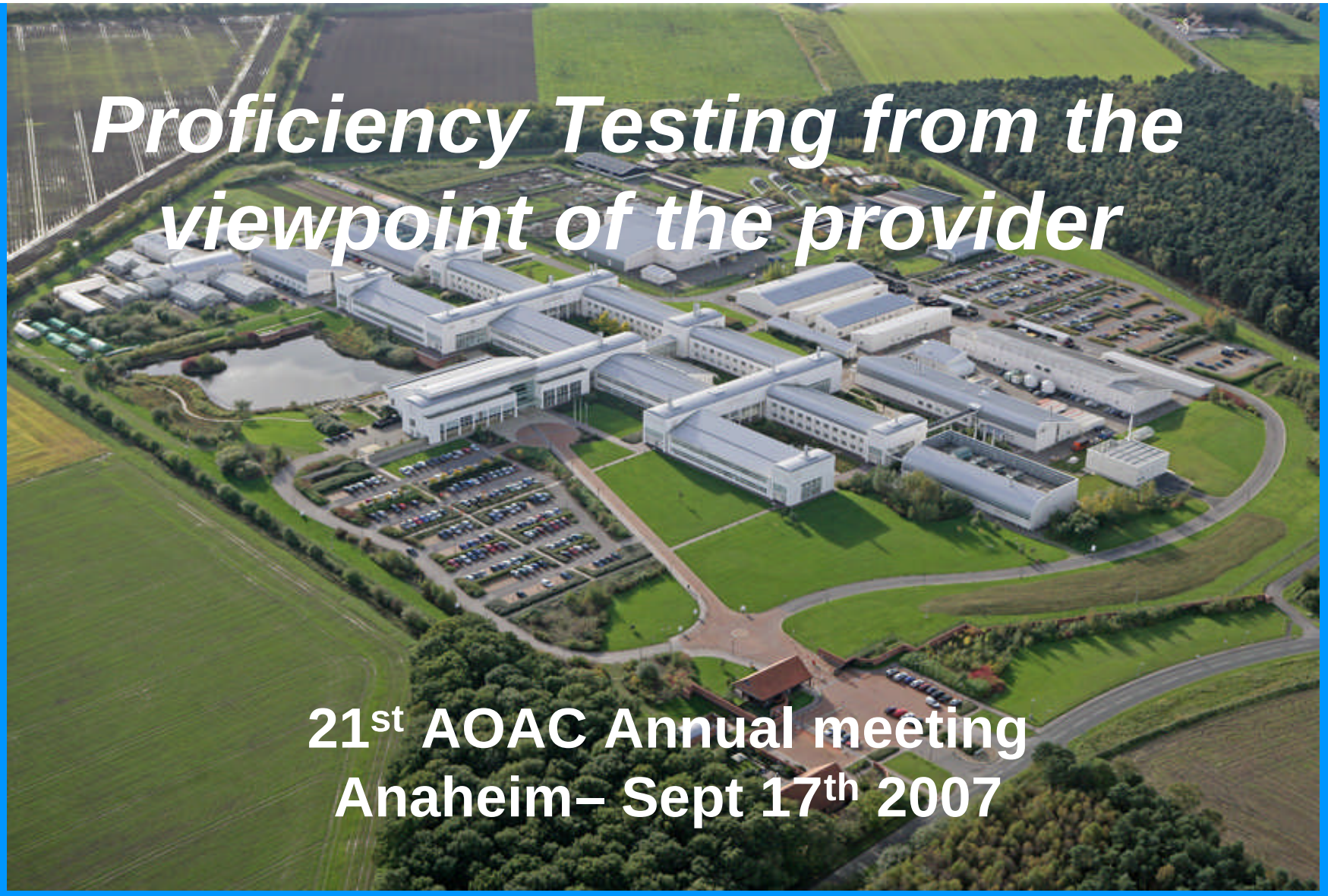


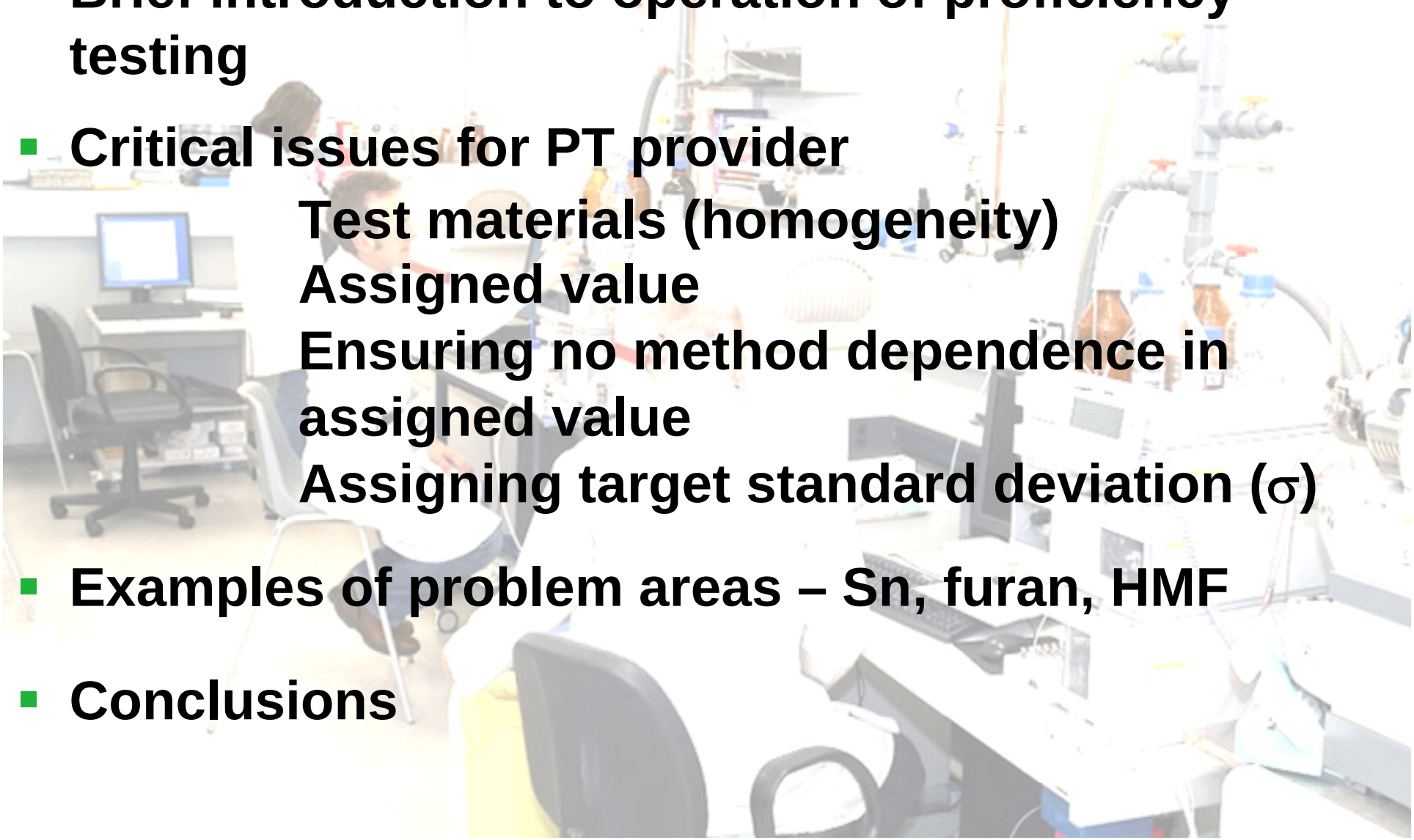
Proficiency Testing from the viewpoint of the provider

21st AOAC Annual meeting
Anaheim– Sept 17th 2007

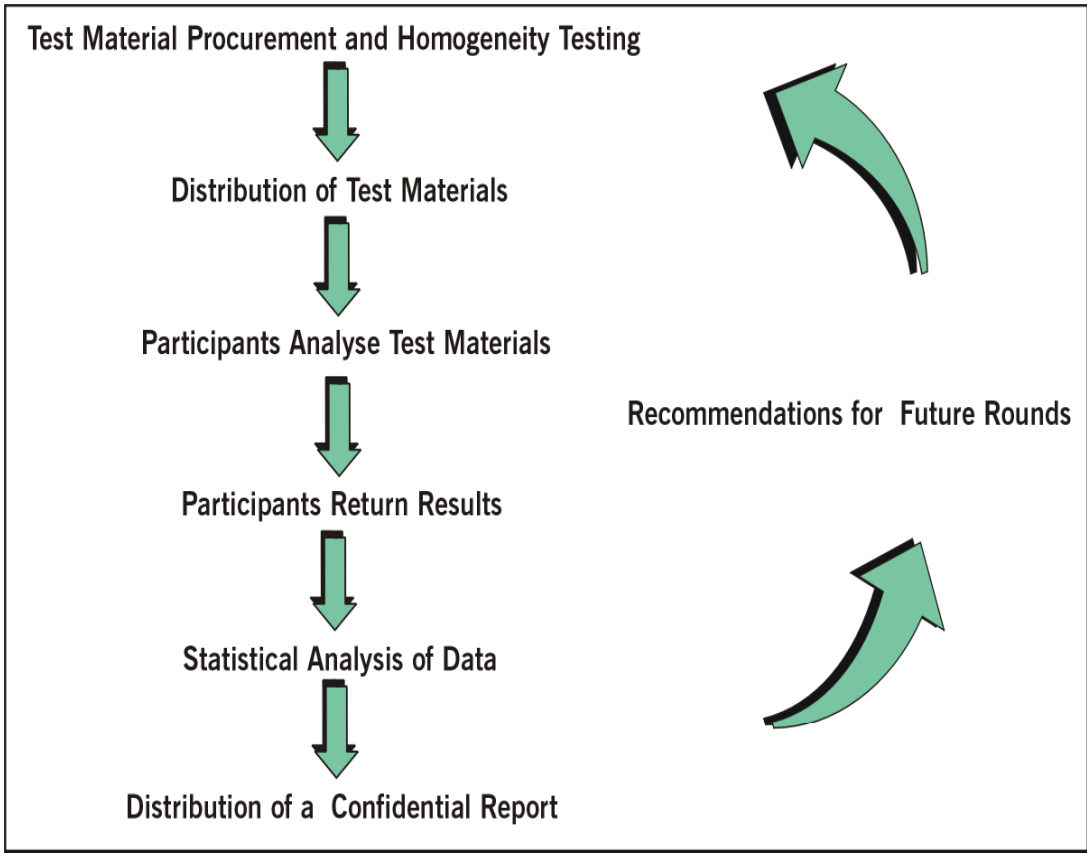
John Gilbert – Science Director
Central Science laboratory
j.gilbert@csl.gov.uk

Outline of Talk

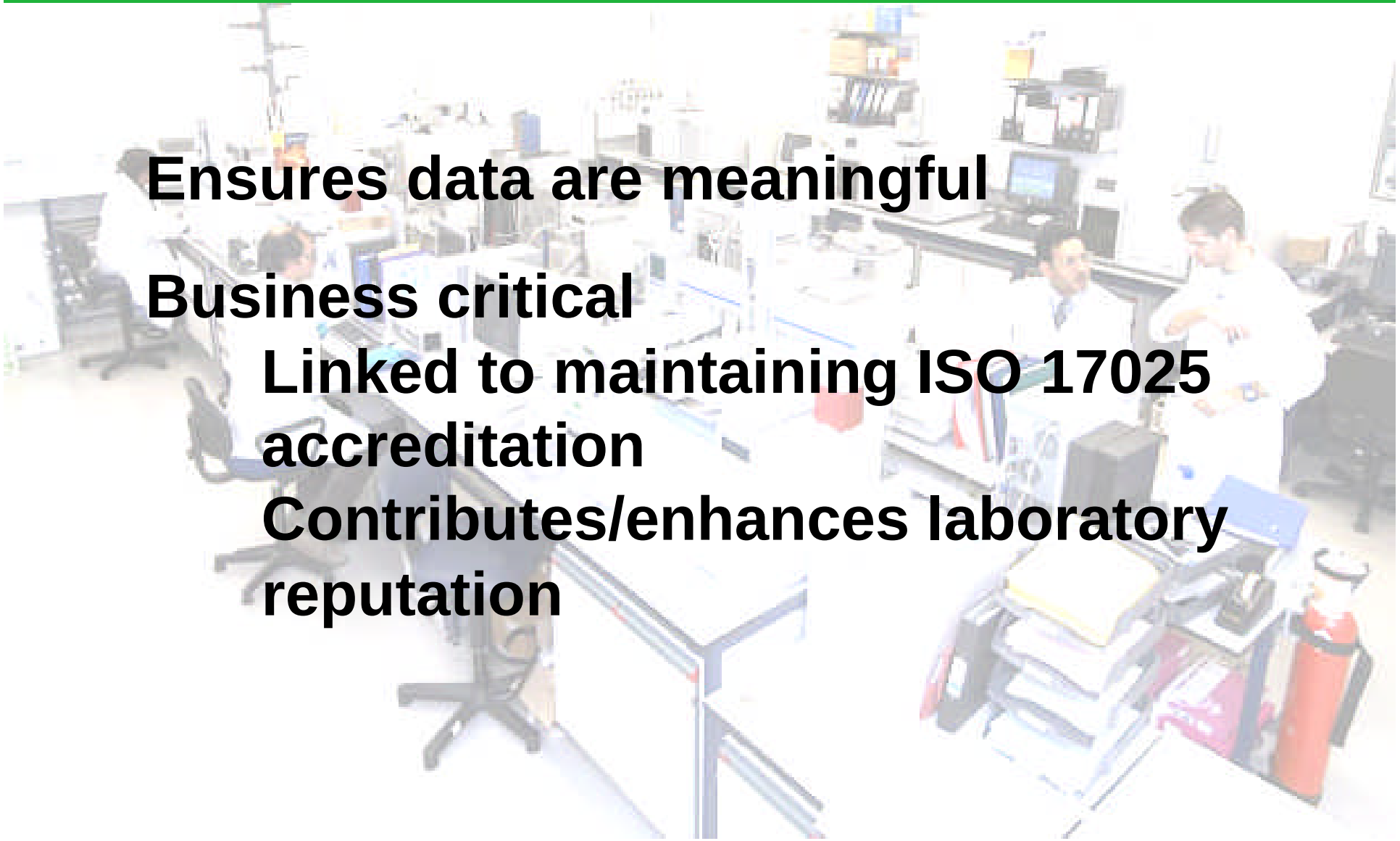
- Brief introduction to operation of proficiency testing
- Critical issues for PT provider
  - Test materials (homogeneity)
  - Assigned value
  - Ensuring no method dependence in assigned value
  - Assigning target standard deviation (σ)
- Examples of problem areas – Sn, furan, HMF
- Conclusions



Organisation of FAPAS



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)

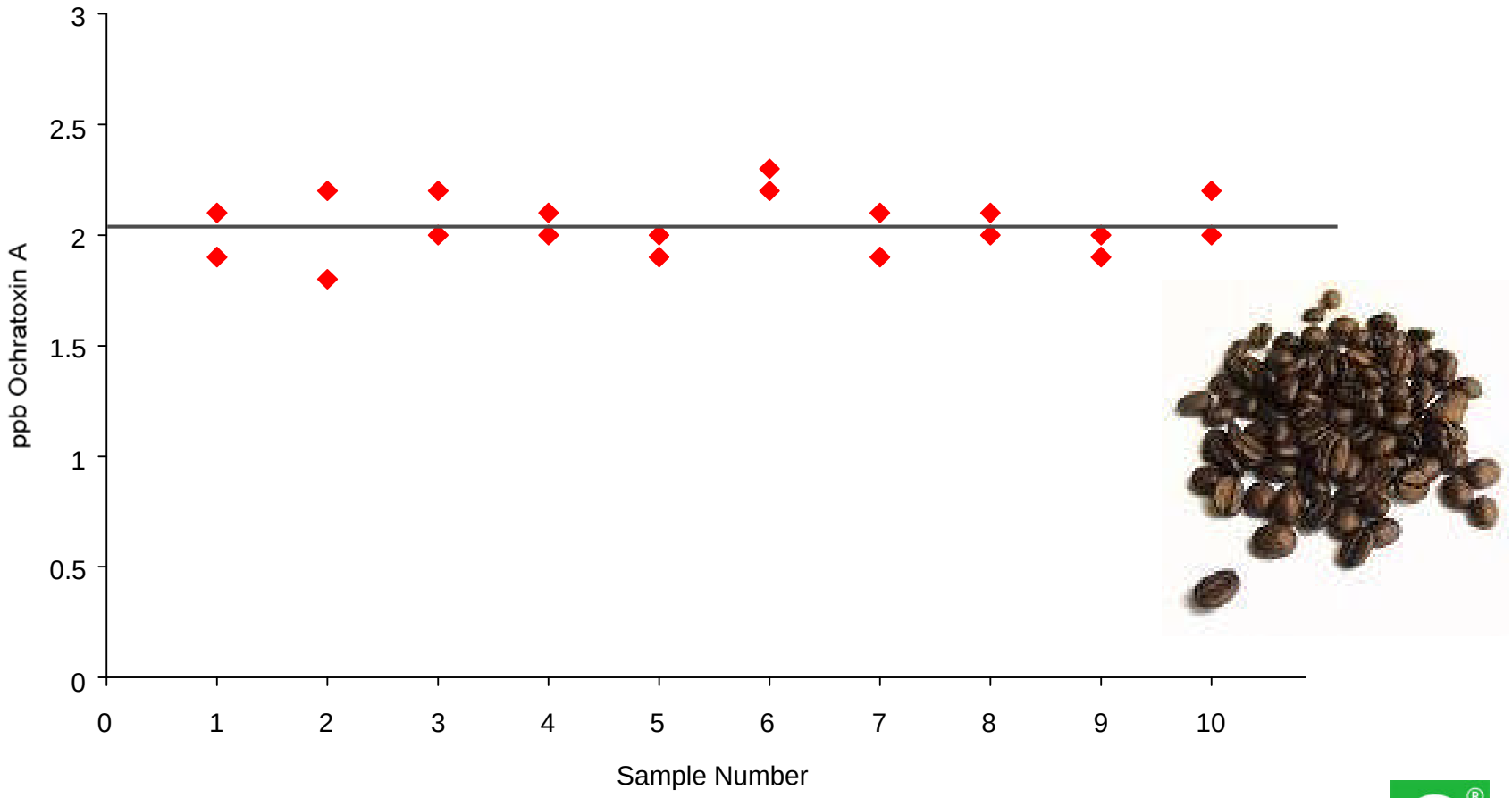
-time-consuming and expensive to prepare

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

$$z = (x - \hat{x}) / \sigma$$

where x = reported value of analyte

$\hat{x}$ = assigned value of analyte - 'true' concentration

σ = target value for standard deviation of values of x

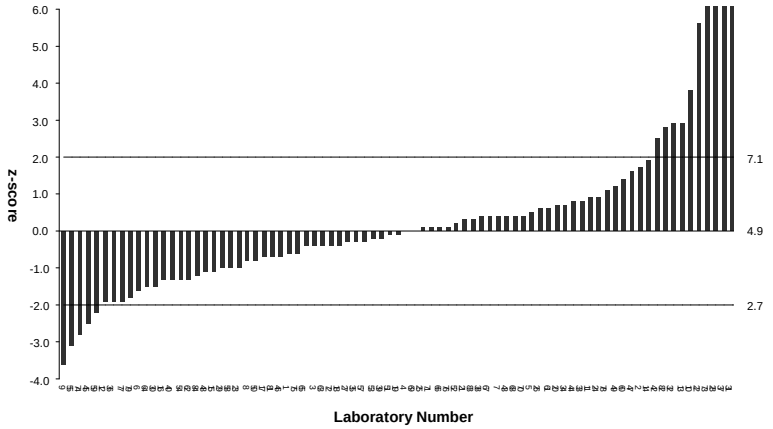
$z = \leq 2$ 'Satisfactory' 95% well-behaved results

$2 < z < 3$ 'Questionable'

$z \geq 3$ 'Unsatisfactory'

Example Table and Chart for Aflatoxin B_1

laboratory number	analyte		
	assigned value	AFB_1 4.97	µg/kg
	result µg/kg	recovery %	z-score
001	4.28	68.9	-0.6
002	6.78	100	1.7
003	4.5	106	-0.4
004	5.0	86	0.0
005	5.56	88.6	0.5
006	3.2	80	-1.6
007	5.4	95.6	0.4
008	4.07	81.8	-0.8
009	1.0	96	**-3.6**
010	9.1	63.65	**3.8**
011	6.0	75	0.9
012	2.9	79.2	-1.9
013	8.20	101.62	**2.9**
014	7.09	103	1.9
015	3.82	113	-1.1



Target Standard Deviation

- 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

	Acceptable range ppb	Numbers of participants		% Satisfactory
		Satisfactory	Unsatisfactory	
Horwitz	11.3 - 39.6	102	19	84
95% ±2 z-score	2.4 - 48.4	114	7	95
Best practice	15.8 - 35.1	86	35	71

True value and assigned value

- ‘True’ value is an ideal
- ‘Assigned value’ is the best estimate of the determinand

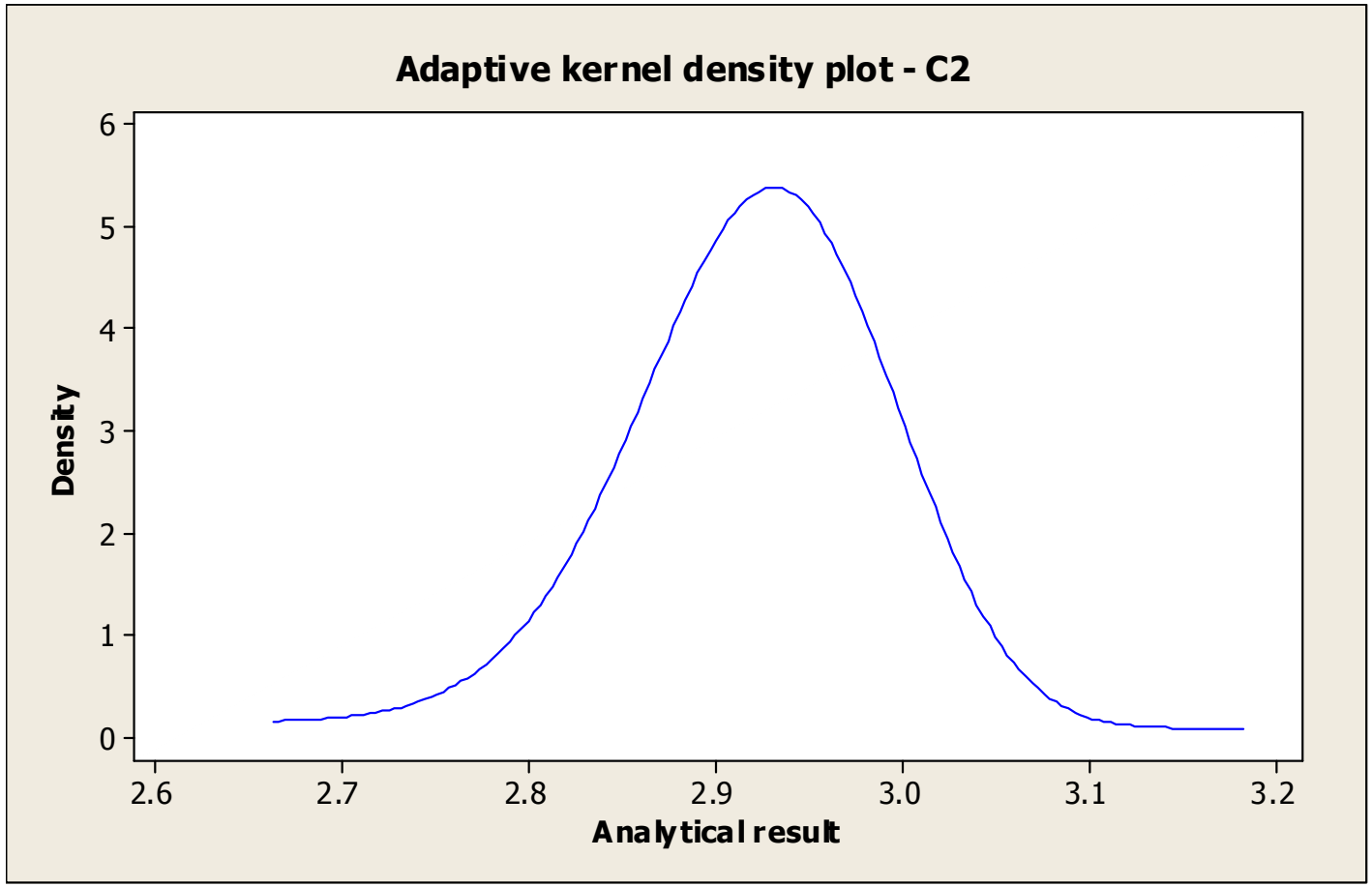
The Assigned Value

- FAPAS® derives the assigned value from the most appropriate measure of central tendency:
  - robust mean
  - median
  - mode

To satisfy PT Participants organisers MUST:-

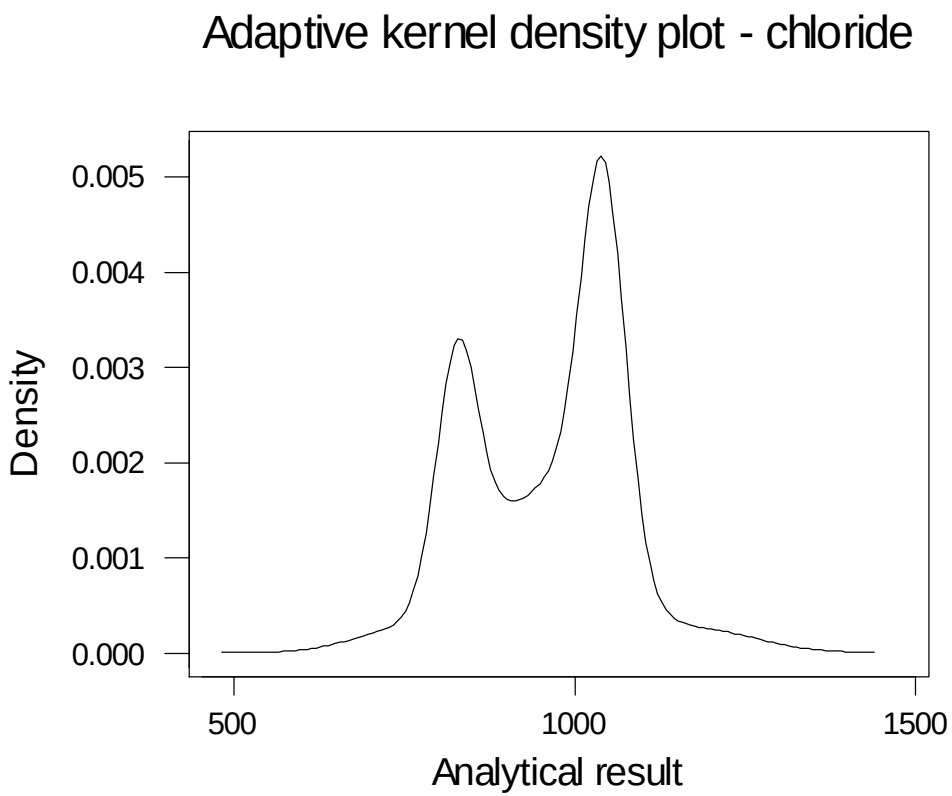
- Be confident in assigned value
- Be confident that there is no method dependence in dataset
  - bump-hunting

‘Bump-hunting’ for the Mode(s)



Lowthian & Thompson (2002) *Analyst*, 127: 1359

Bimodal Results – Poor Methodology?

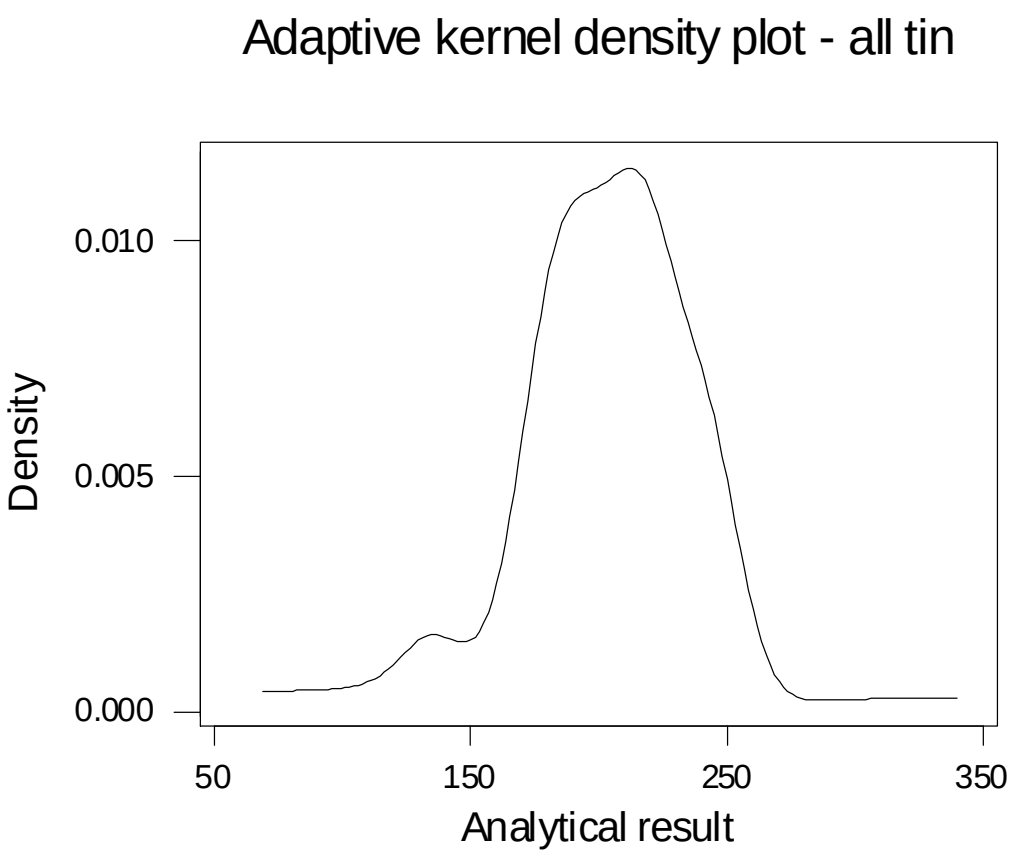


FAPAS 0738 – Tin in Tomato Paste

- 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



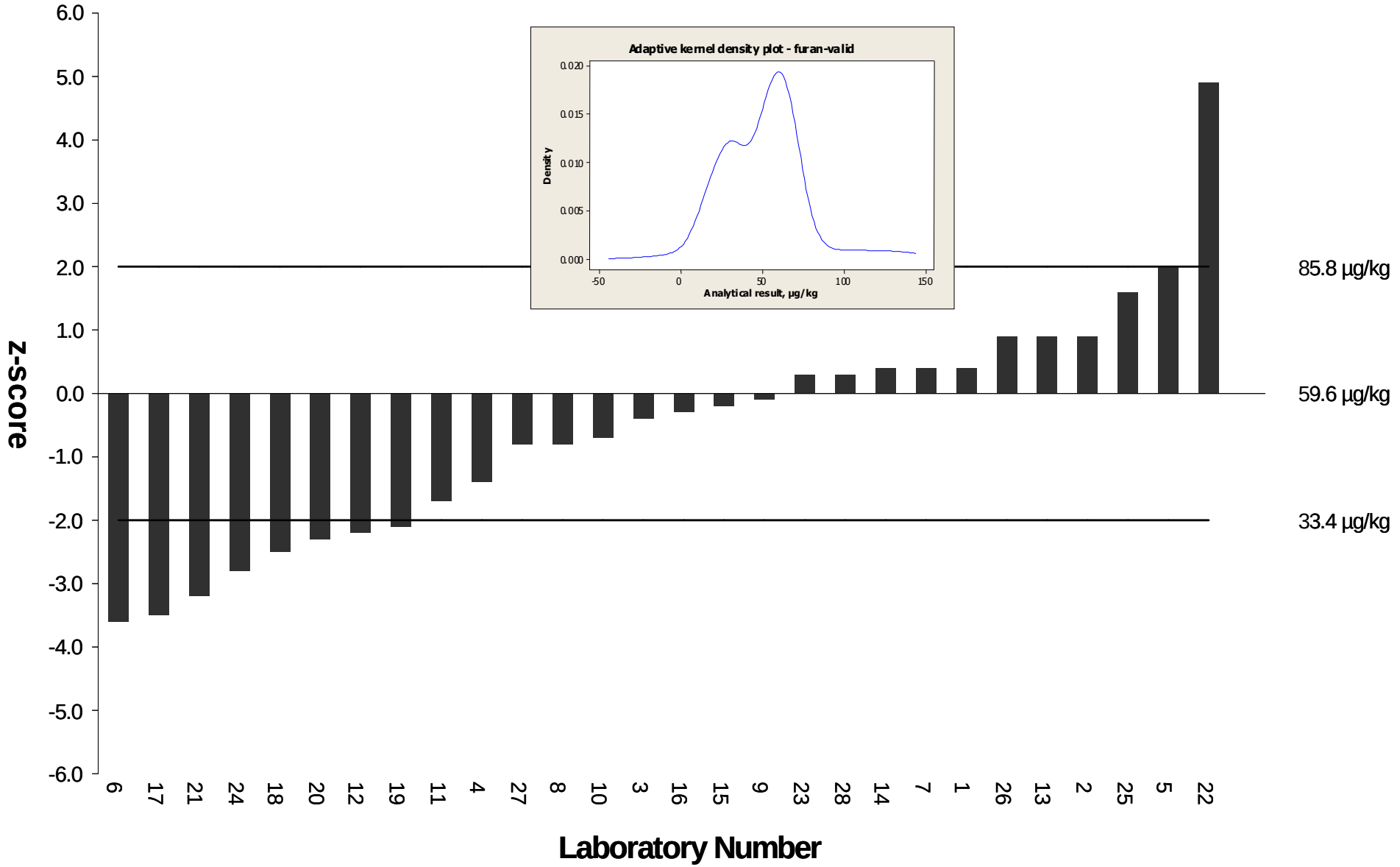
Issues with PT for tin analysis

- 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

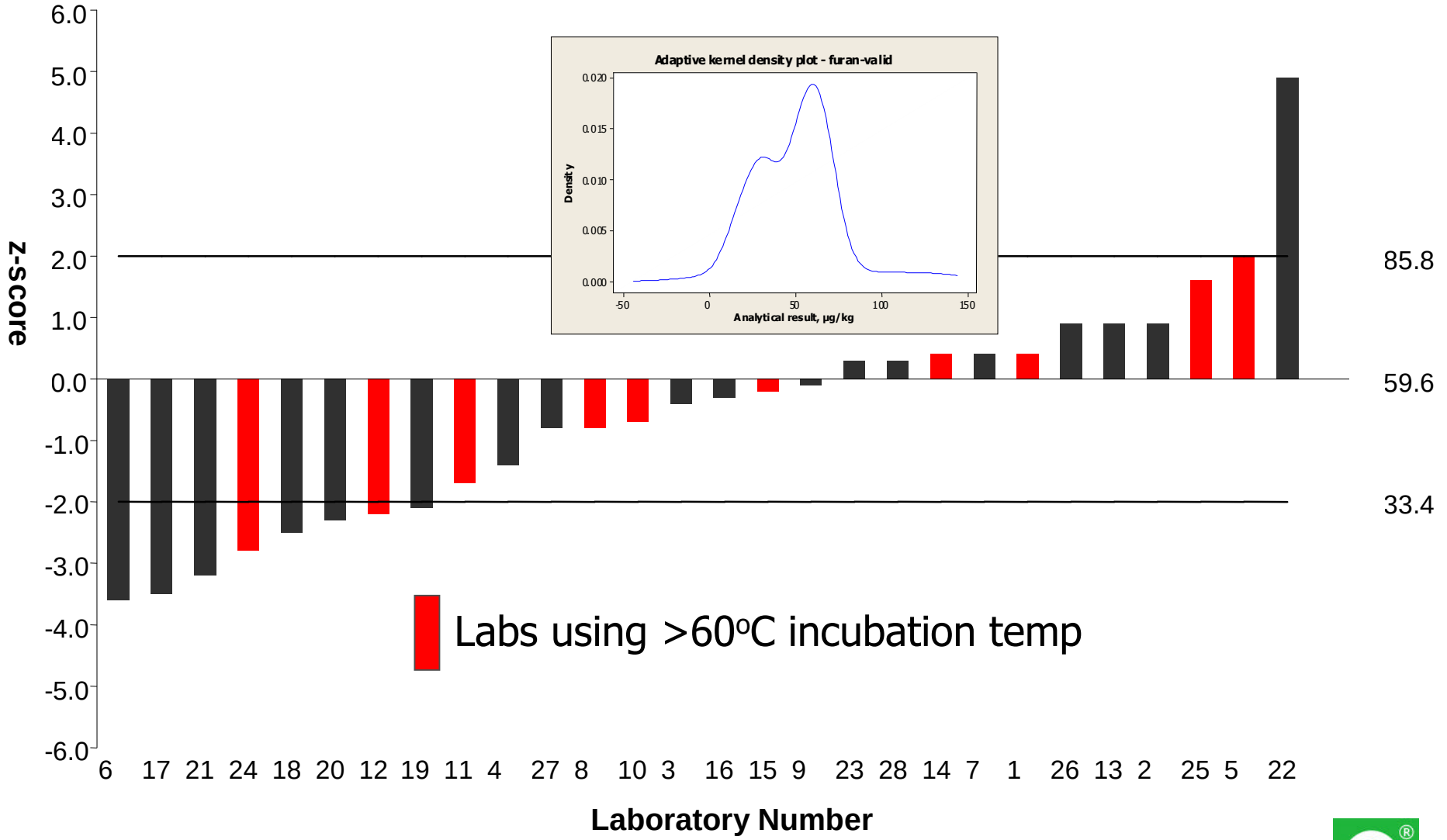
Analysis of furan in babyfood

- 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

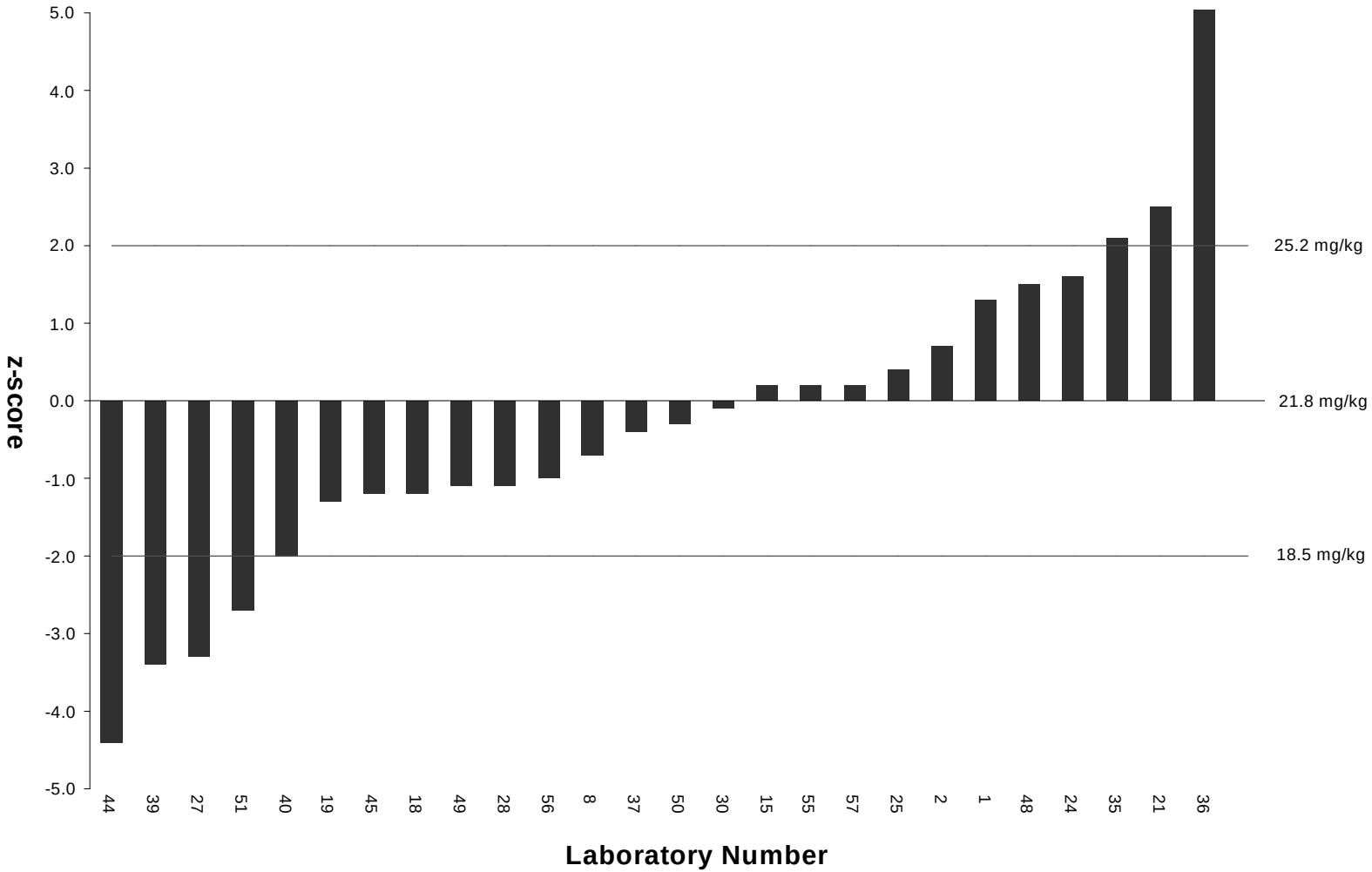


Hydroxymethylfurfural (HMF)

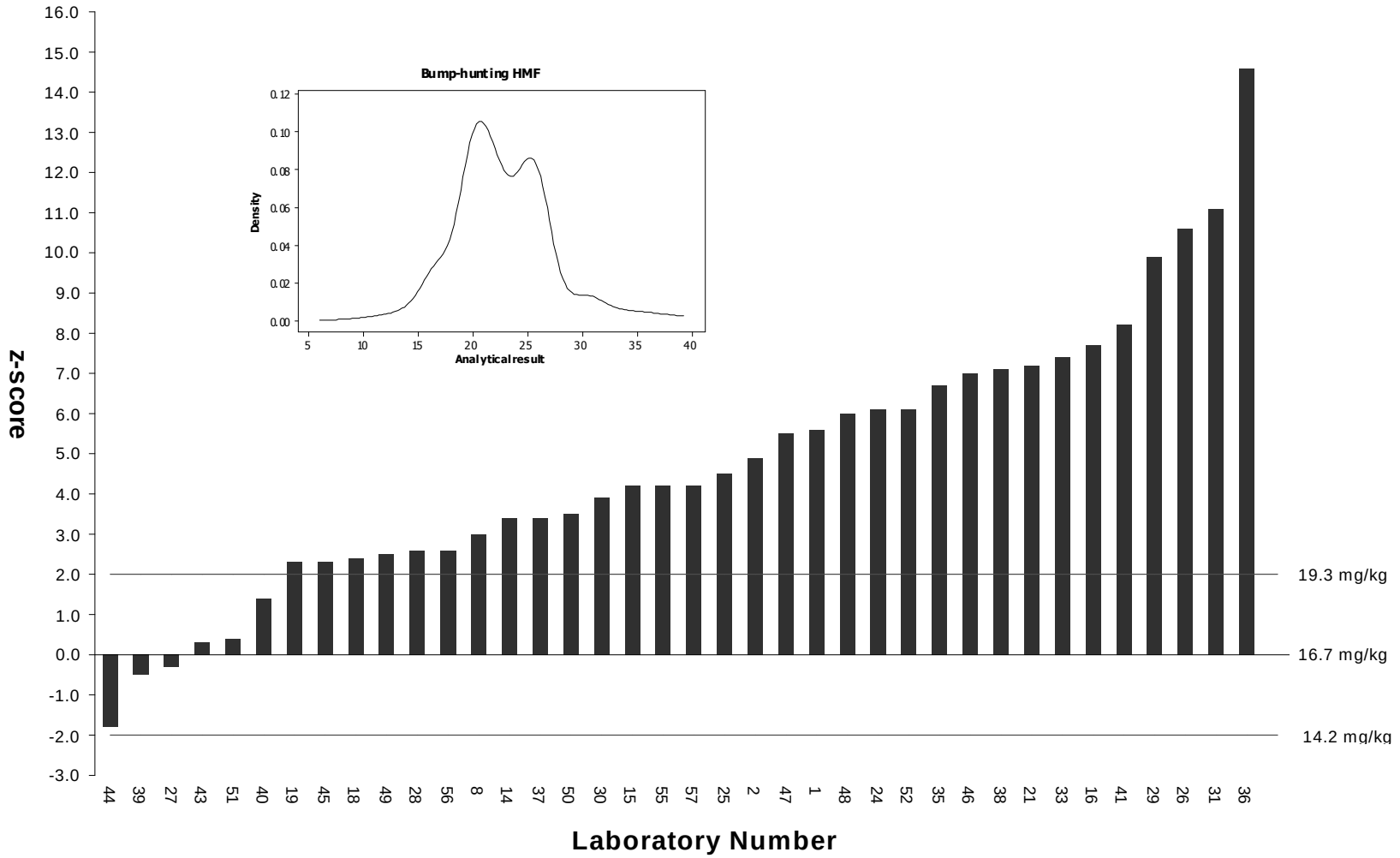
- HMF – quality indicator in honey (Regulatory limit <40 mg/kg)

- 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



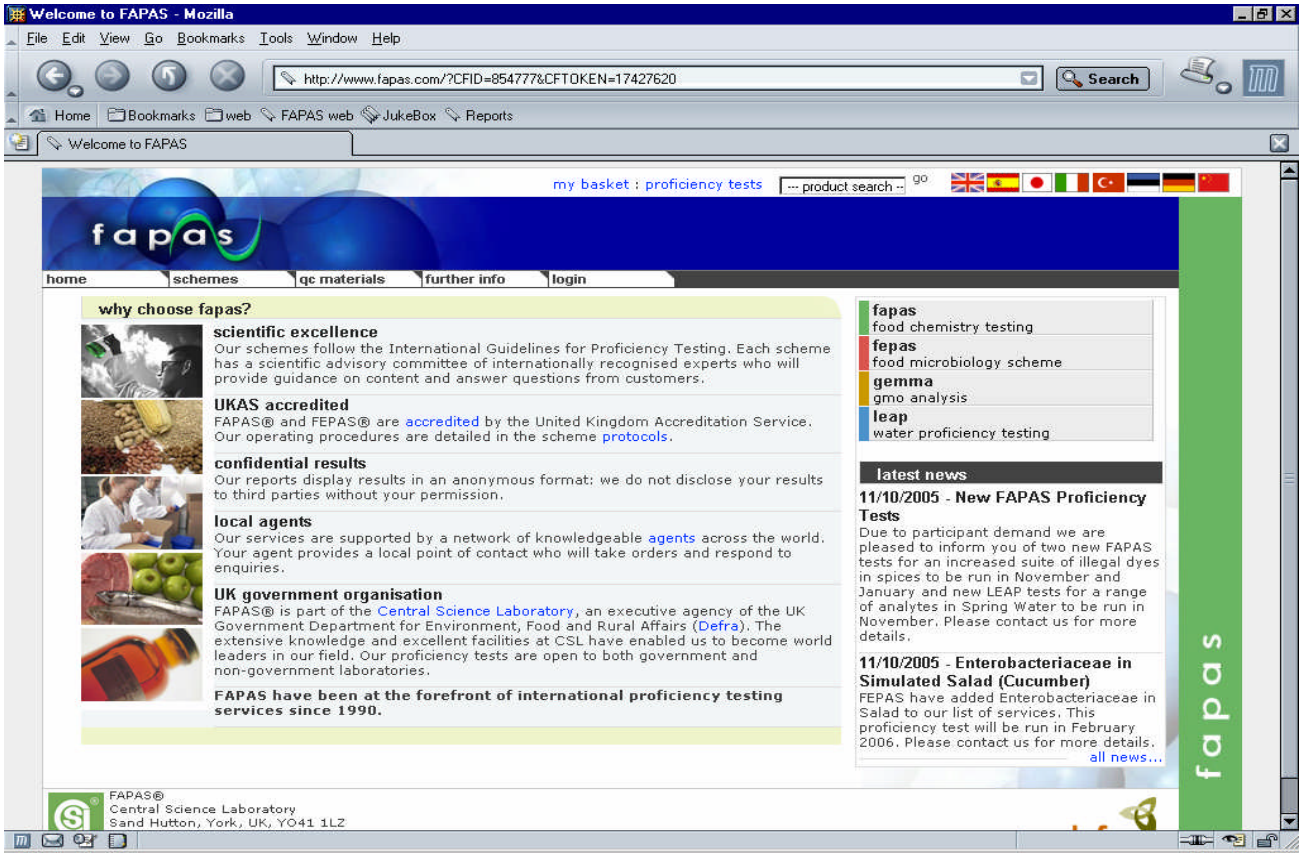
Gokmen & Senyuva (2006) ***J. Agric Food Chem 54: 2845***

(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™

Tel: +44 (0)1904 462100

Fax:+44 (0)1904 462111

E-mail: fapas@csl.gov.uk

www.fapas.com