



*Proficiency Testing from the  
viewpoint of the provider*

**21<sup>st</sup> AOAC Annual meeting  
Anaheim– Sept 17<sup>th</sup> 2007**

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Central Science laboratory

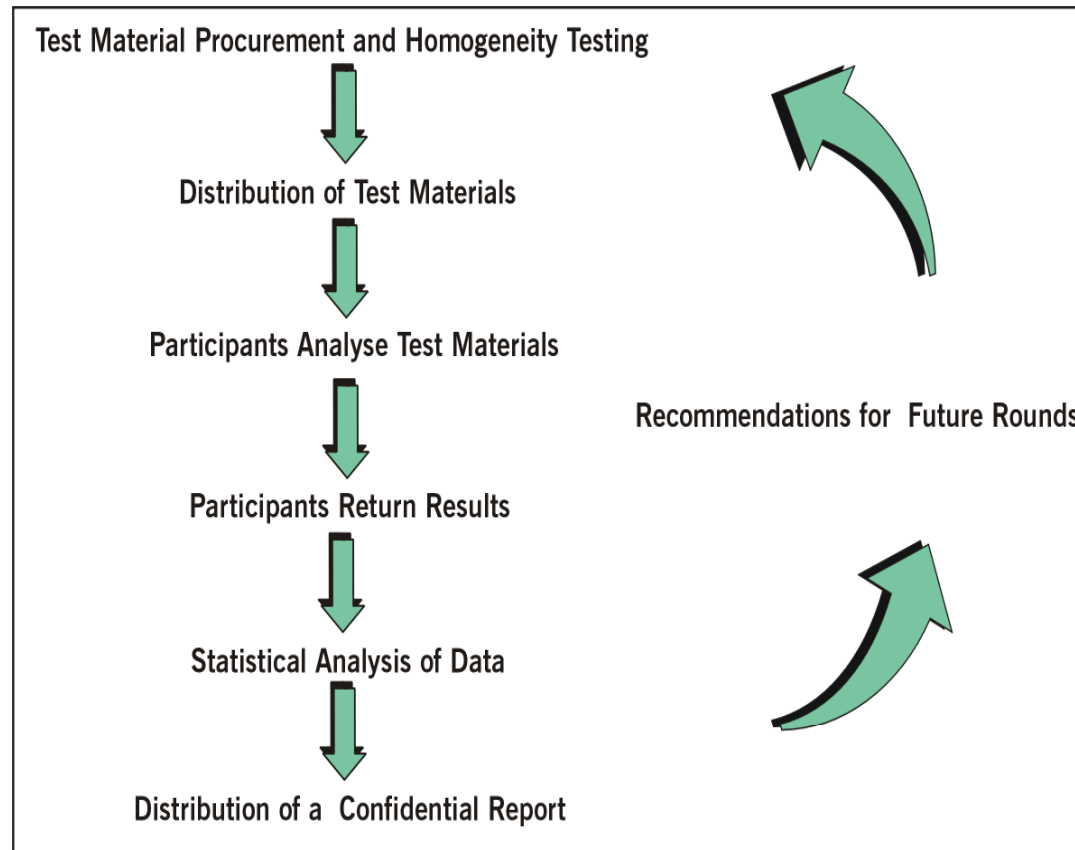
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# Outline of Talk

- **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



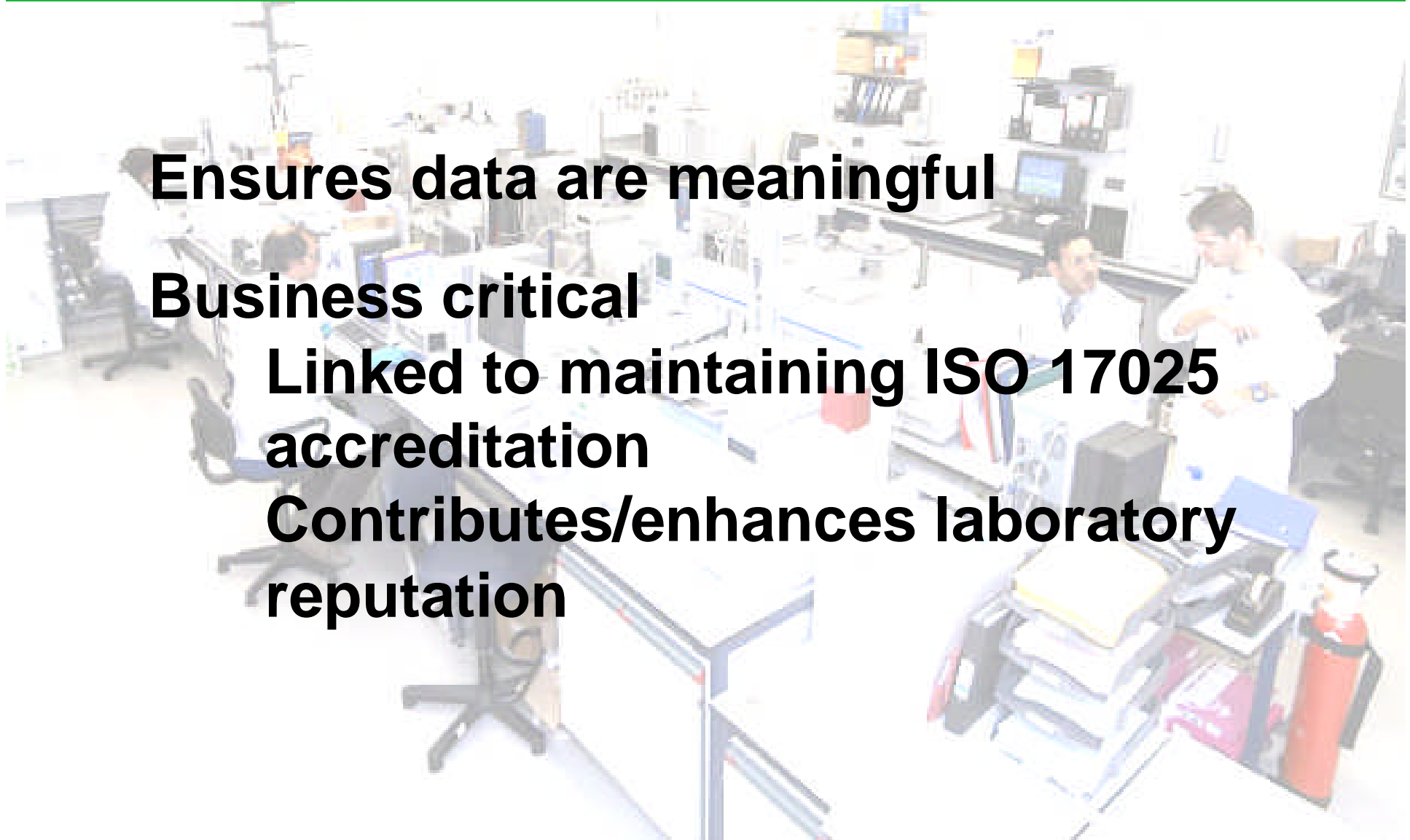
# Importance of PT to participants

**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

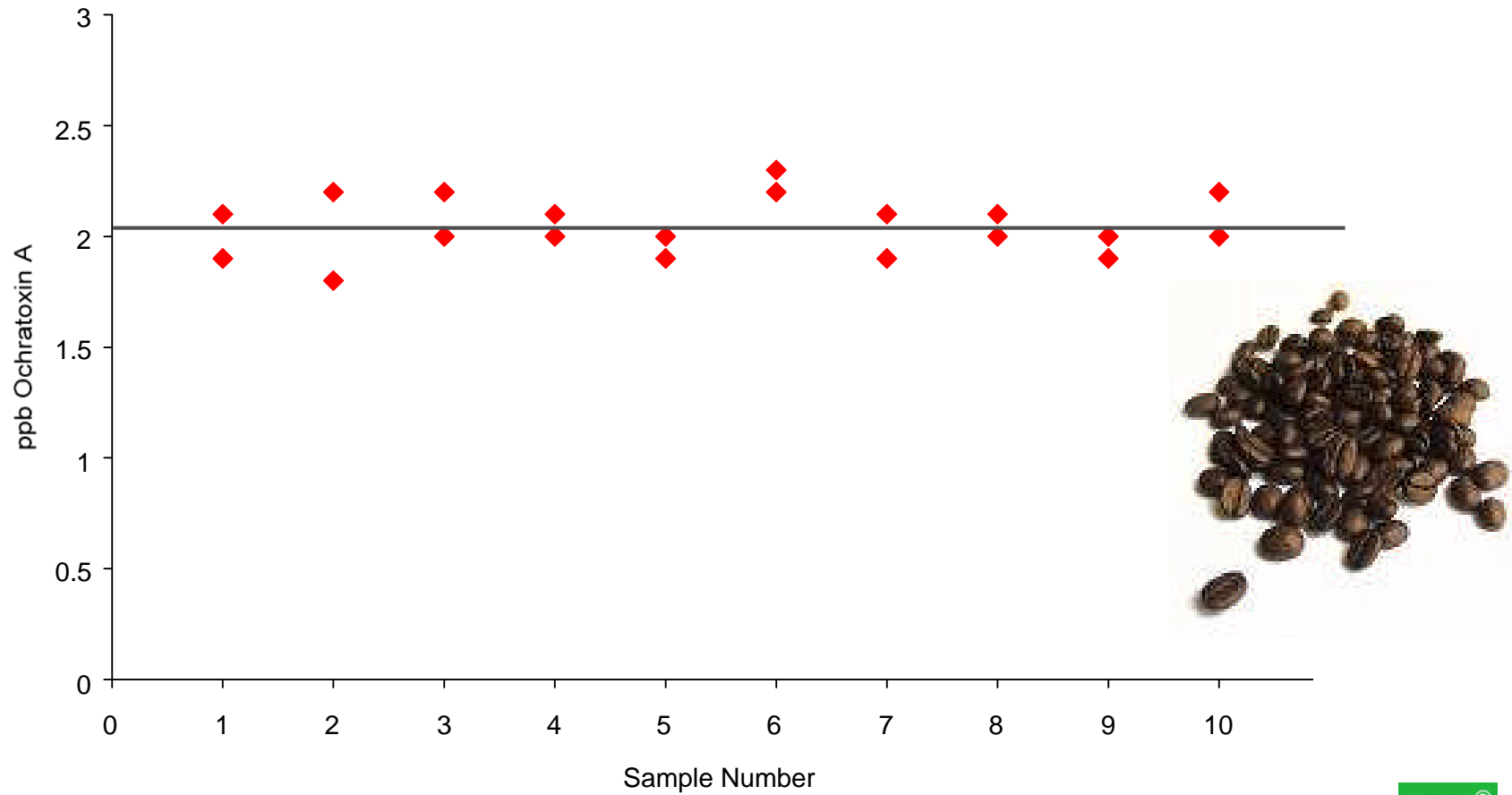
Need to have confidence in analyte stability over 3-6 months

Need to be able to prepare in homogenised form

Need to demonstrate homogeneity



# FAPAS<sup>®</sup> 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

$\sigma$  = target value for standard deviation of values of  $x$

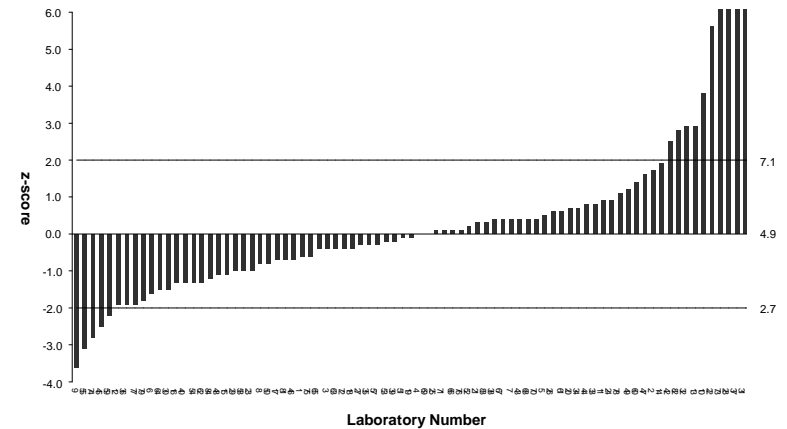
- $z = \leq 2$  'Satisfactory' 95% well-behaved results
- $2 < z < 3$  'Questionable'
- $z \geq 3$  'Unsatisfactory'





# Example Table and Chart for Aflatoxin B<sub>1</sub>

laboratory number	analyte		
	assigned value	AFB <sub>1</sub>	
		4.97	μg/kg
result	recovery	z-score	
μg/kg	%		
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	<b>-3.6</b>
010	9.1	63.65	<b>3.8</b>
011	6.0	75	0.9
012	2.9	79.2	-1.9
013	8.20	101.62	<b>2.9</b>
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 $\sigma$ -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% $\pm 2$ z-score	2.4 - 48.4	114	7	95
Best practice	15.8 - 35.1	86	35	71

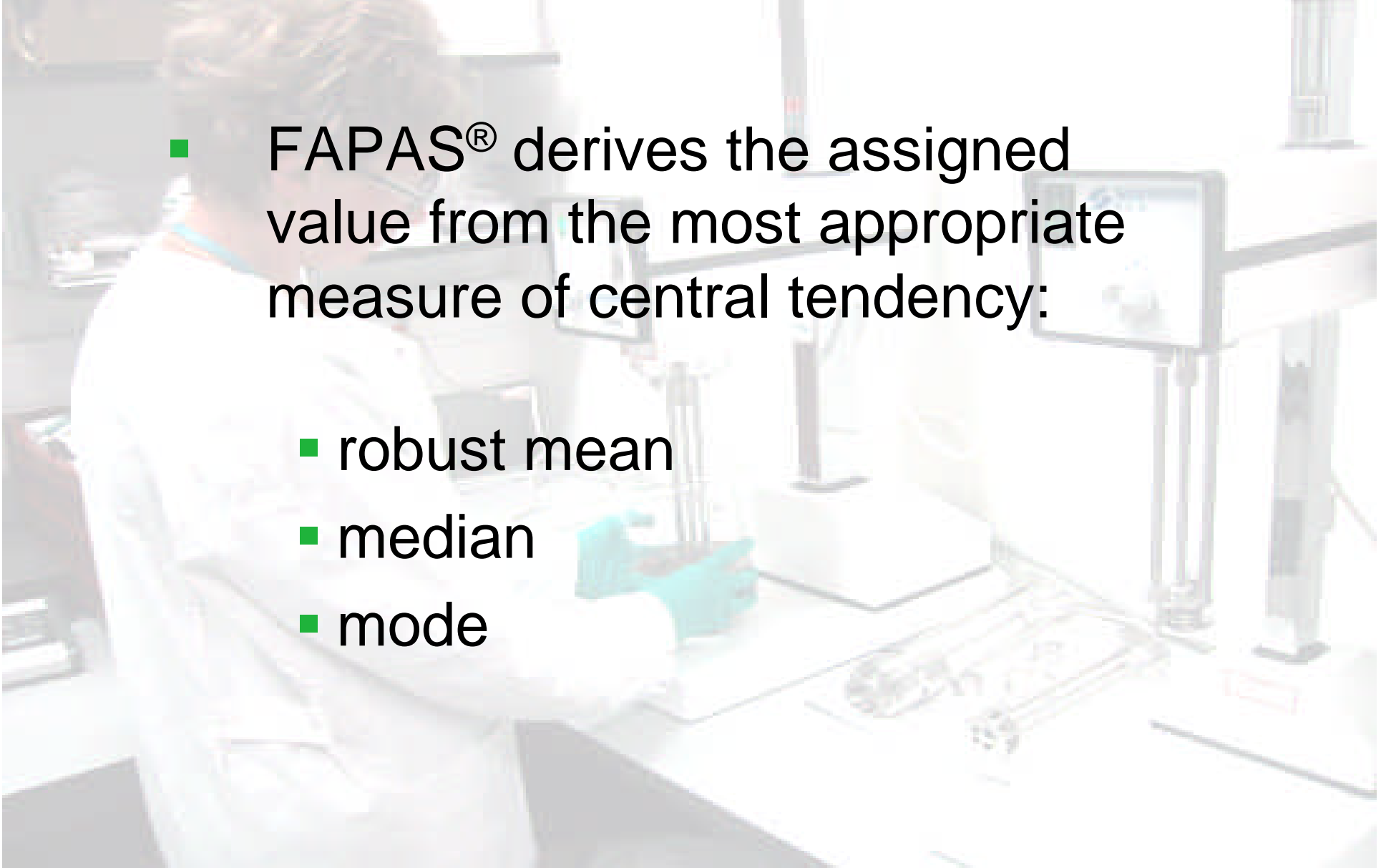
# True value and assigned value

- **'True' value is an ideal**
- **'Assigned value' is the best estimate of the determinand**



# The Assigned Value

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

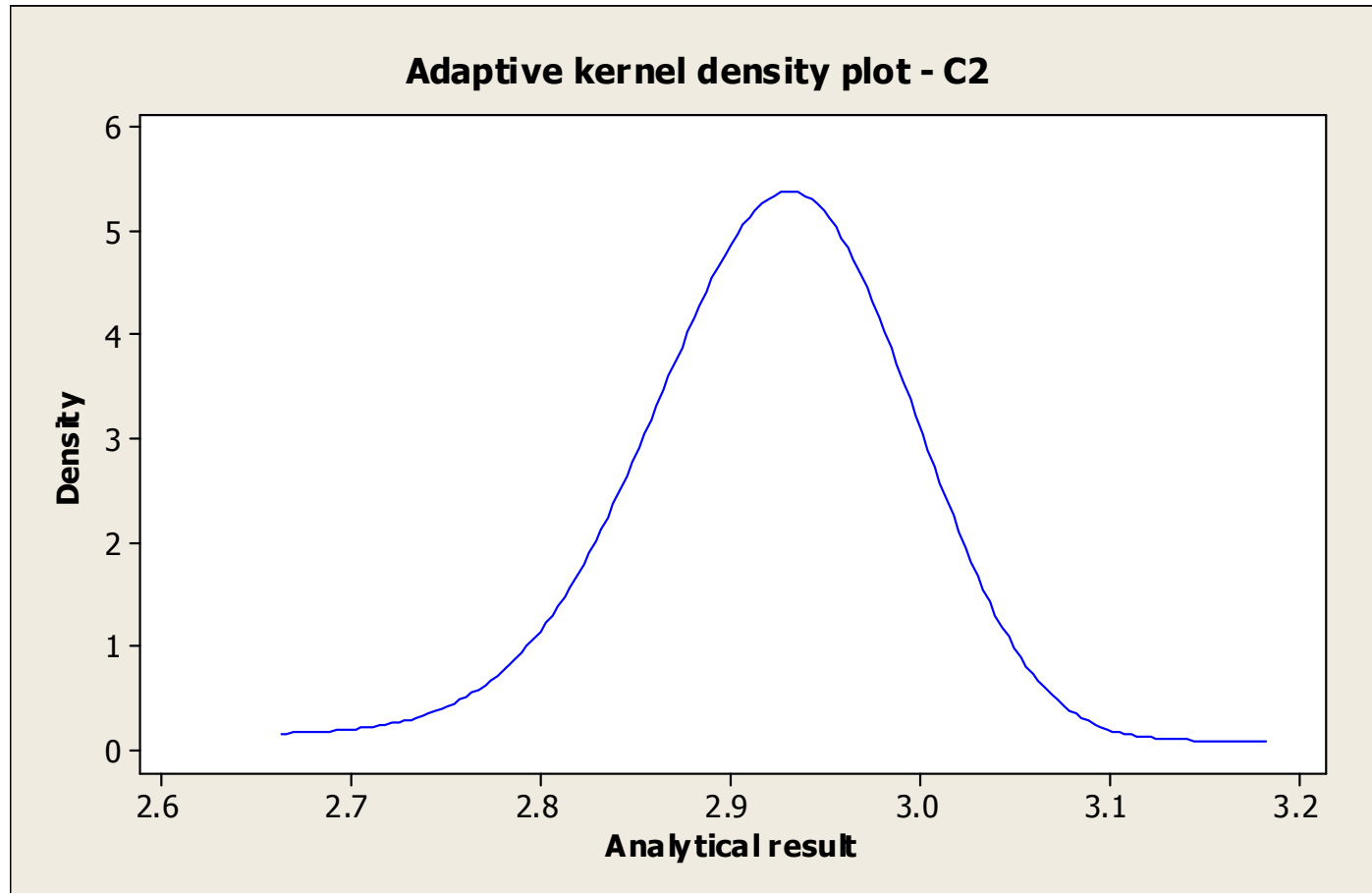


## To satisfy PT Participants organisers MUST:-

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



# 'Bump-hunting' for the Mode(s)

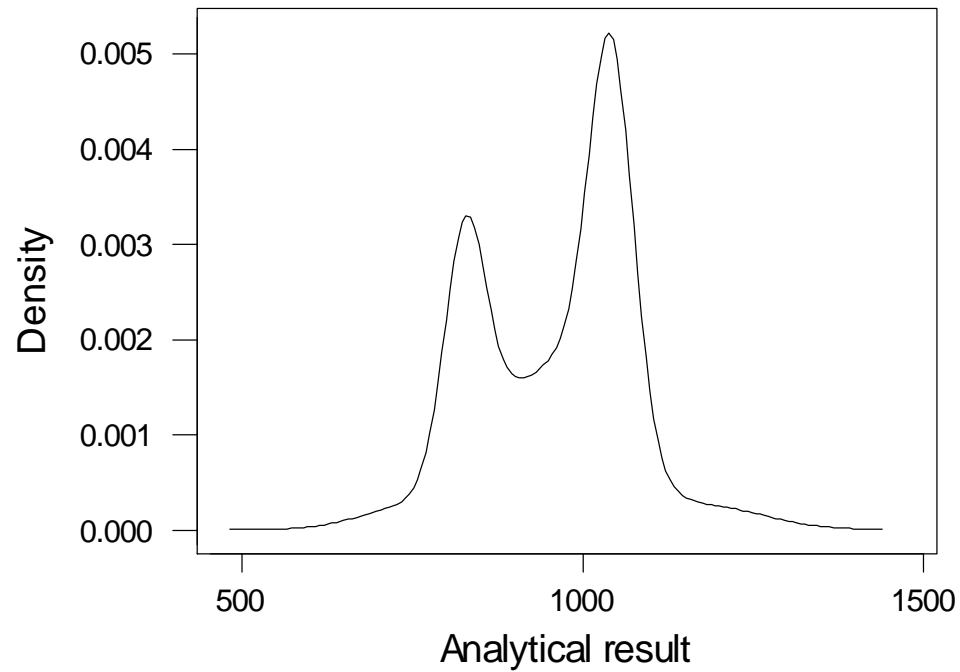


Lowthian & Thompson (2002) *Analyst*, 127: 1359



# Bimodal Results – Poor Methodology?

Adaptive kernel density plot - chloride





# FAPAS 0738 – Tin in Tomato Paste

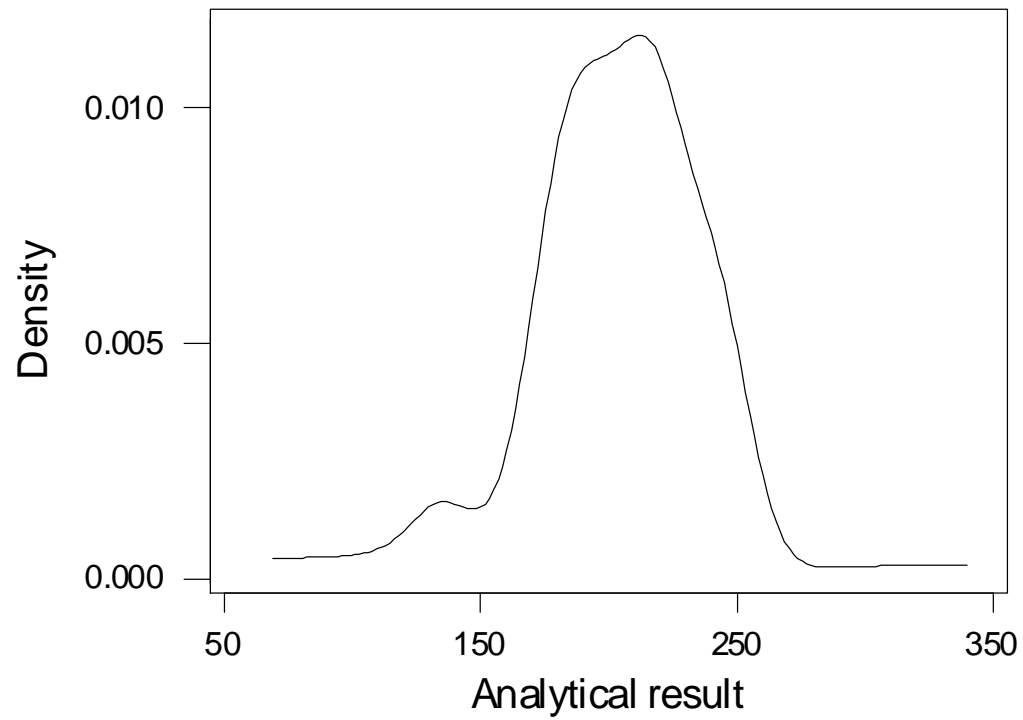
- Preparation
  - Spiked at 250 mg/kg
  - Homogeneity mean was 251 mg/kg
- Results from participants
  - Consensus of results was 204 mg/kg
  - Consensus was 20% lower than the spike
  - Homogeneity mean would have resulted in a z-score of 3.2
  - Using ICP-IDMS result was 247.8 mg/kg



# 0738 – Tin in Tomato Paste



Adaptive kernel density plot - all tin



# 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

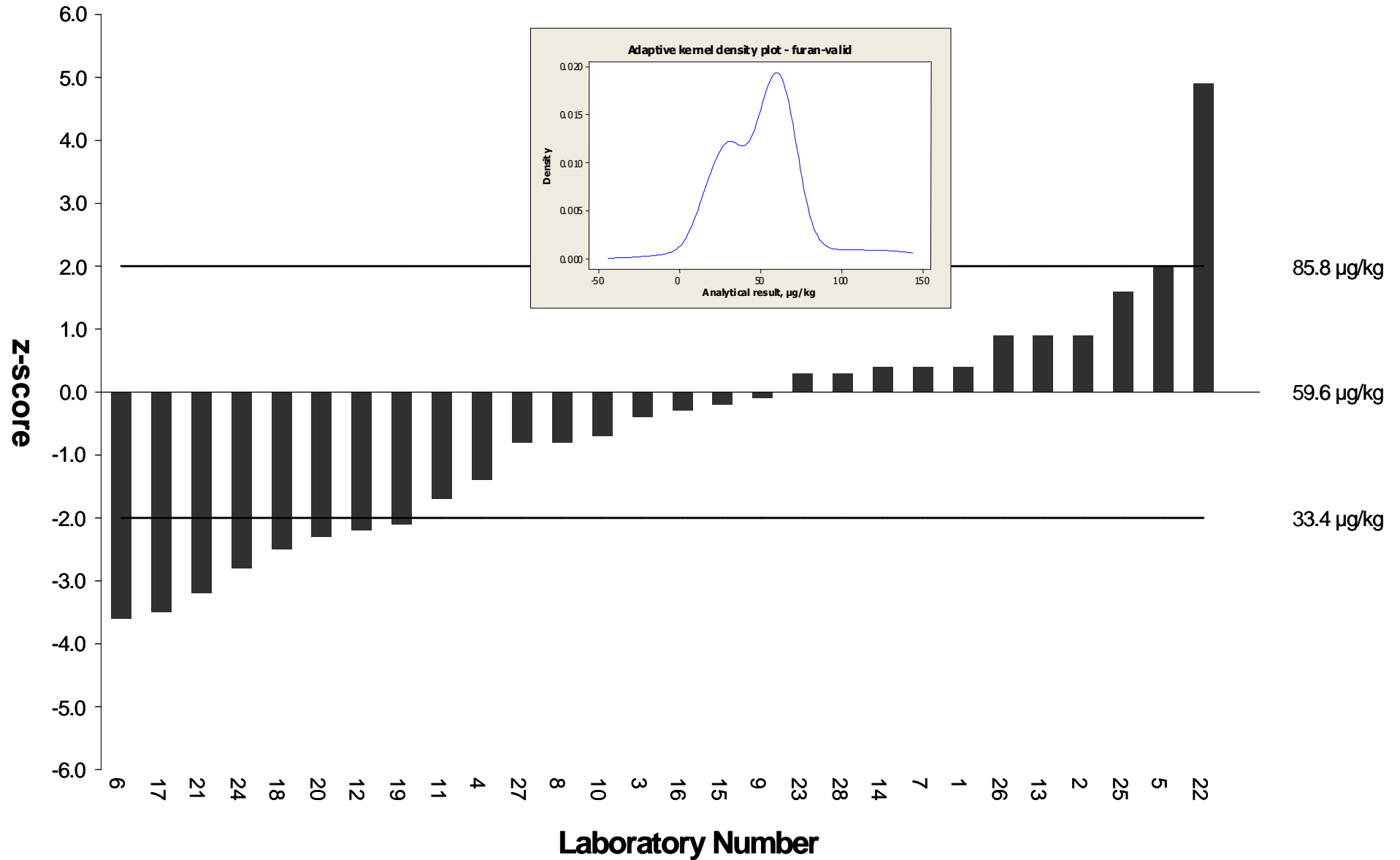


# Analysis of furan in babyfood

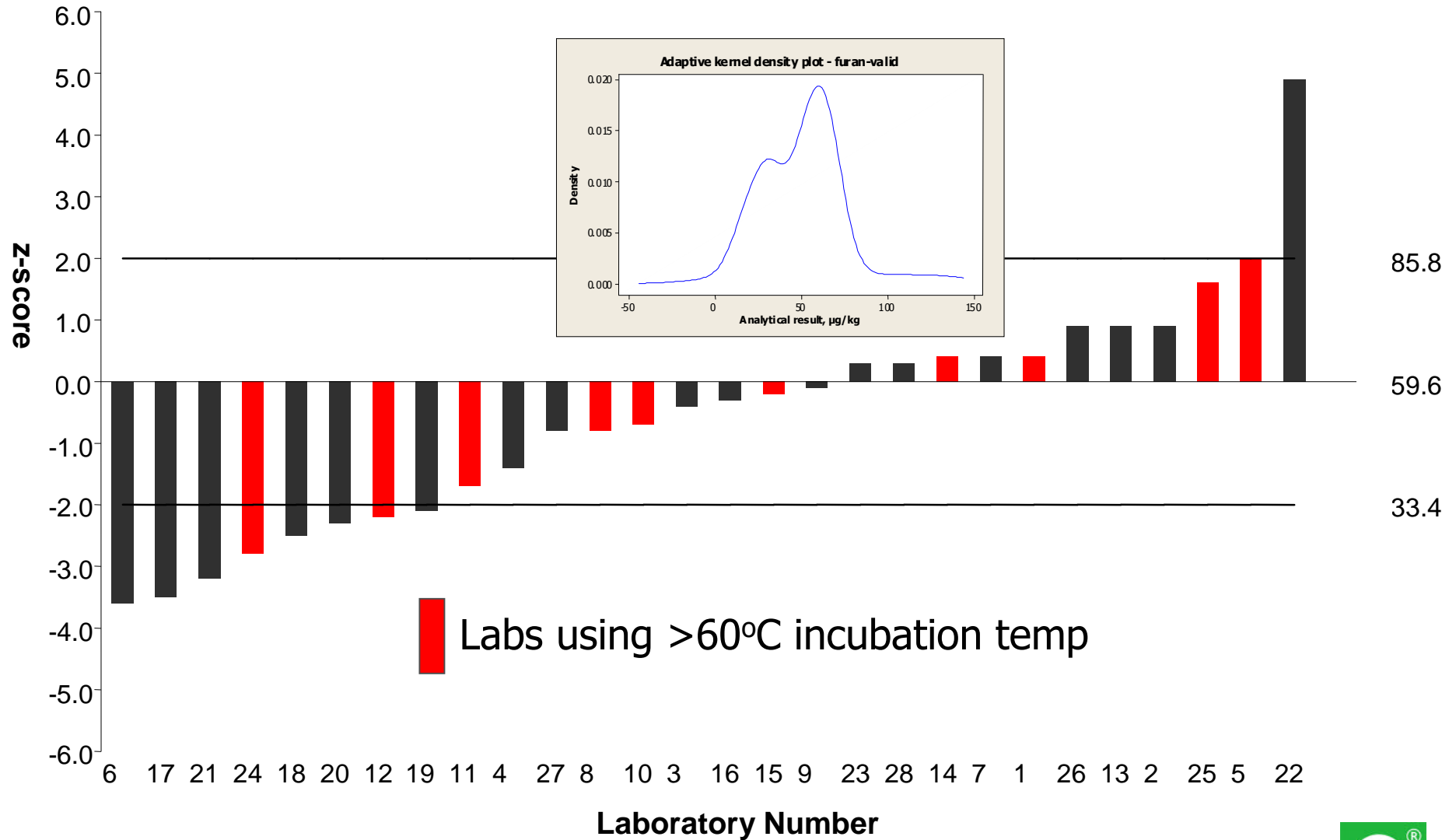
- Furan – b.p. 31.4 °C
- Heat processing contaminant found in canned and jarred products e.g. baby food, soups, coffee and fruit juices.
- Analysis:-
  - Static Headspace GC/MS or solid phase micro-extraction (SPME)-GC/MS
  - Isotope dilution methodology with [ $^2\text{H}_4$ ]-furan as internal standard



# Z-Scores for Furan (59.6 $\mu\text{g}/\text{kg}$ ) in Baby Food



# Z-Scores for Furan (59.6 µg/kg) in Baby Food

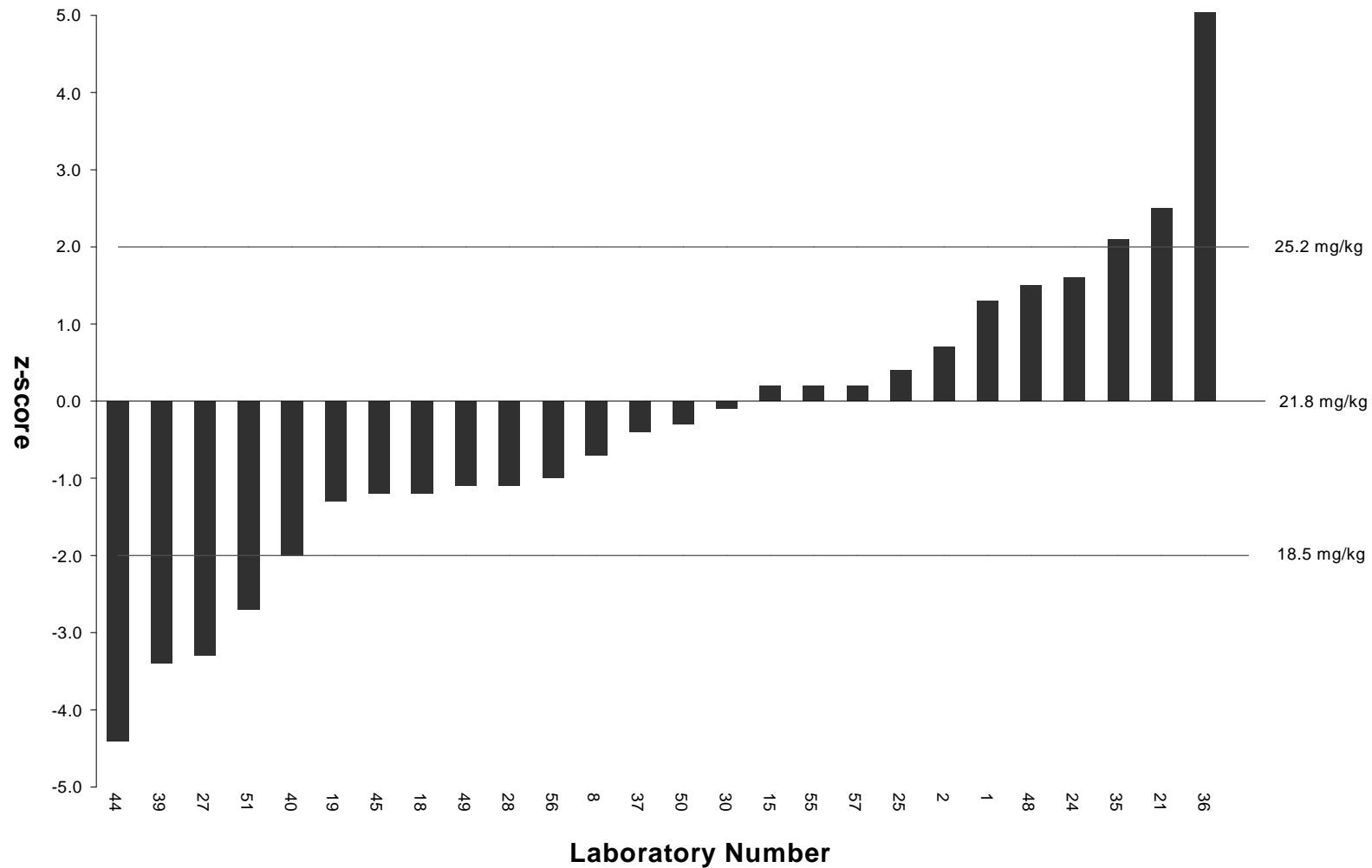


# Hydroxymethylfurfural (HMF)

- HMF – quality indicator in honey (Regulatory limit <40 mg/kg)
- Analysis:-
  - Colorimetric method
  - HPLC – no clean-up
  - HPLC – SPE clean-up

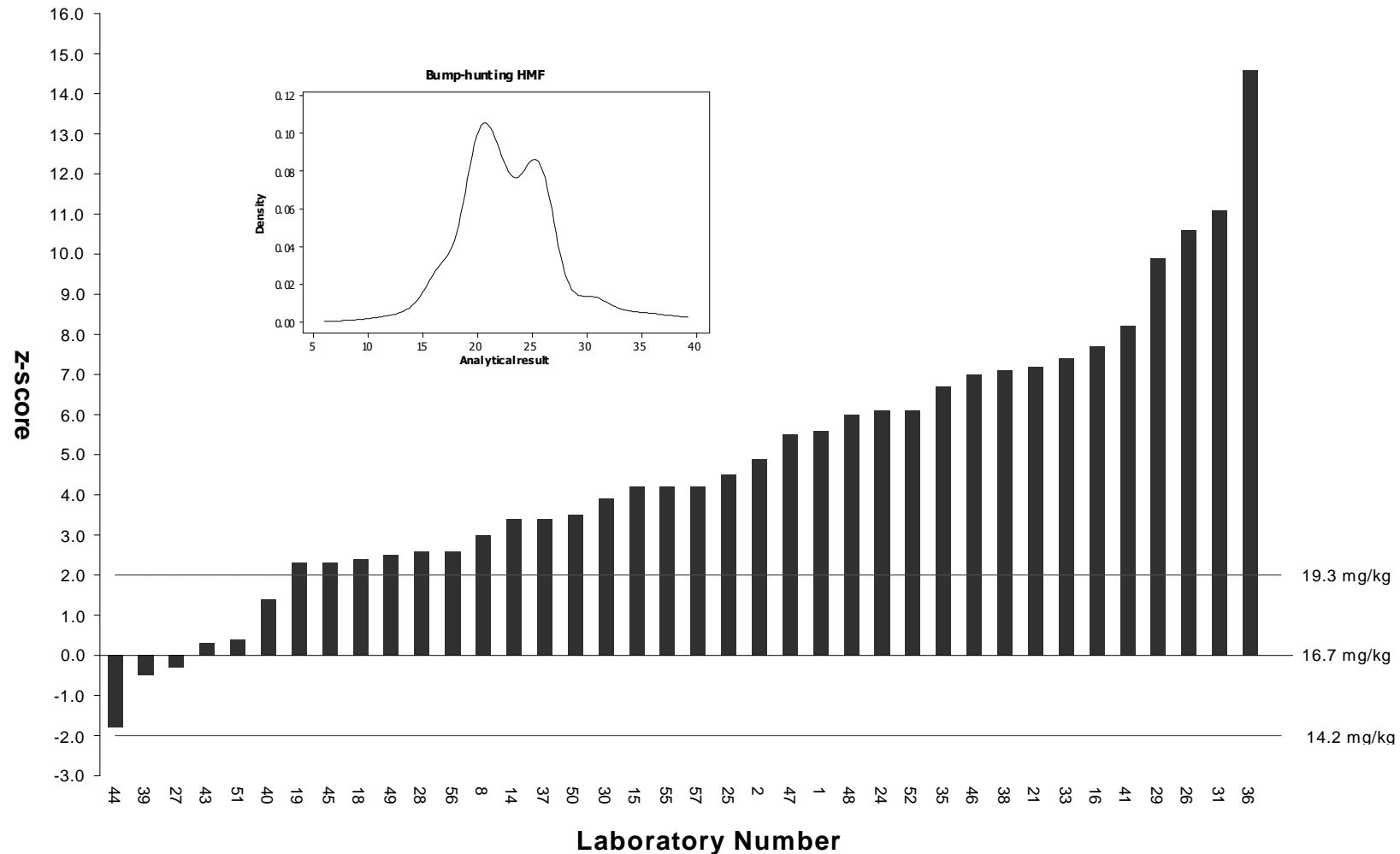


# Z-Scores for HMF by HPLC without SPE clean-up (21.8 mg/kg) in honey





# 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

The screenshot shows a Mozilla browser window displaying the FAPAS website. The address bar shows the URL: <http://www.fapas.com/?CFID=854777&CFTOKEN=17427620>. The website features a blue header with the FAPAS logo and navigation links: home, schemes, qc materials, further info, and login. A search bar is located in the top right corner. The main content area is divided into several sections:

- why choose fapas?**
  - scientific excellence**: Our schemes follow the International Guidelines for Proficiency Testing. Each scheme has a scientific advisory committee of internationally recognised experts who will provide guidance on content and answer questions from customers.
  - UKAS accredited**: FAPAS® and FEPAS® are accredited by the United Kingdom Accreditation Service. Our operating procedures are detailed in the scheme protocols.
  - confidential results**: Our reports display results in an anonymous format: we do not disclose your results to third parties without your permission.
  - local agents**: Our services are supported by a network of knowledgeable agents across the world. Your agent provides a local point of contact who will take orders and respond to enquiries.
  - UK government organisation**: FAPAS® is part of the Central Science Laboratory, an executive agency of the UK Government Department for Environment, Food and Rural Affairs (Defra). The extensive knowledge and excellent facilities at CSL have enabled us to become world leaders in our field. Our proficiency tests are open to both government and non-government laboratories.
- FAPAS have been at the forefront of international proficiency testing services since 1990.**
- latest news**
  - 11/10/2005 - New FAPAS Proficiency Tests**: Due to participant demand we are pleased to inform you of two new FAPAS tests for an increased suite of illegal dyes in spices to be run in November and January and new LEAP tests for a range of analytes in Spring Water to be run in November. Please contact us for more details.
  - 11/10/2005 - Enterobacteriaceae in Simulated Salad (Cucumber)**: FEPAS have added Enterobacteriaceae in Salad to our list of services. This proficiency test will be run in February 2006. Please contact us for more details. [all news...](#)

The footer contains the FAPAS® logo and contact information: Central Science Laboratory, Sand Hutton, York, UK, YO41 1LZ. A vertical green bar with the FAPAS logo is visible on the right side of the page.



## For Further Information, Contact:

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