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The 2006 IUPAC Harmonized Protocol for Proficiency Testing

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NEW!!
IUPAC Harmonized Protocol for Proficiency Testing

Slimmer, Fitter Scoring!!

Detects Multimodal sets!!

Cleaner Homogeneity tests!!

Scope of 2006 IUPAC protocol

- Only chemical analysis.
- Only results obtained on a fitness-for-purpose basis (*i.e.*, suitable for z-scoring with a pre-set value of σ_p).
- Only results on an interval scale or a ratio scale.
- Primarily scientific aspects
  - minimal administrative details
  - no criteria for assessment or accreditation of laboratories or PT schemes.

Properties of an ideal scoring method

- Adds value to raw results
  - Tells you more than just looking at raw data
- Easily understandable
  - e.g. based on the properties of the normal distribution.
- Has no arbitrary scaling transformation.
- Is transferable between different concentrations, analytes, matrices, and measurement principles.

A bad scoring method

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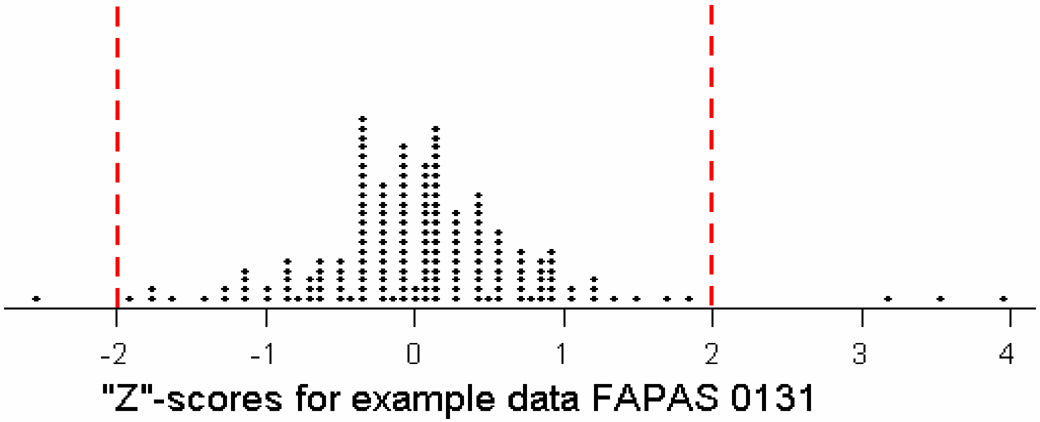
$$z = \left(x - \overline{x}\right) / s$$



$$\overline{x} = 2.126$$

$$s = 0.077$$

97% of scores in range $-2 < z < 2$

- On average, somewhat more than 95% of laboratories receive z-score within the range ±2.

Another weak scoring method

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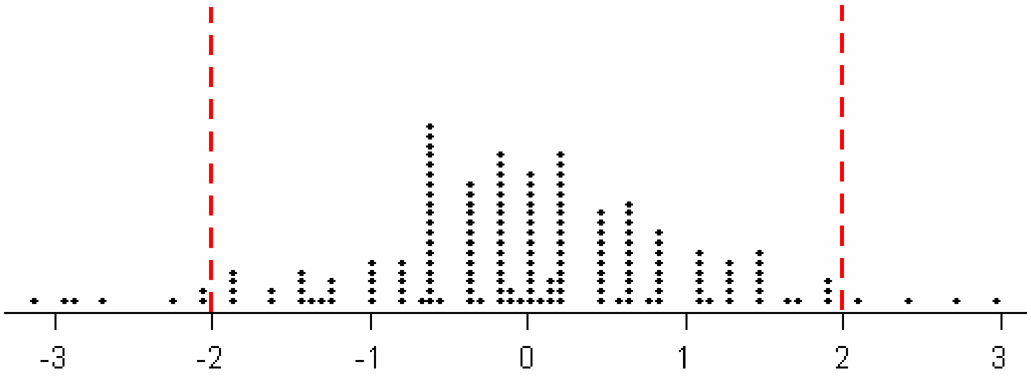
$$z = \left(x - \hat{\mu}_{rob}\right) / \hat{\sigma}_{rob}$$



"Z"-score for example data FAPAS 0131

~91% of data within range -2 < z < 2

$$\hat{\mu}_{rob} = 2.128$$

$$\hat{\sigma}_{rob} = 0.048$$

- On average, slightly less than 95% of laboratories receive a z-score between ±2.

2006 HP Scoring

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- Focuses on the *z*-score

$$z = \left(x - \hat{\mu}_{rob}\right) / \sigma_p \quad \text{where} \quad \sigma_p \equiv u_f$$

- ‘Fit-for-purpose’ scoring basis

$$\sigma_{\mathrm{p}} \equiv u_{\mathrm{ffp}}$$

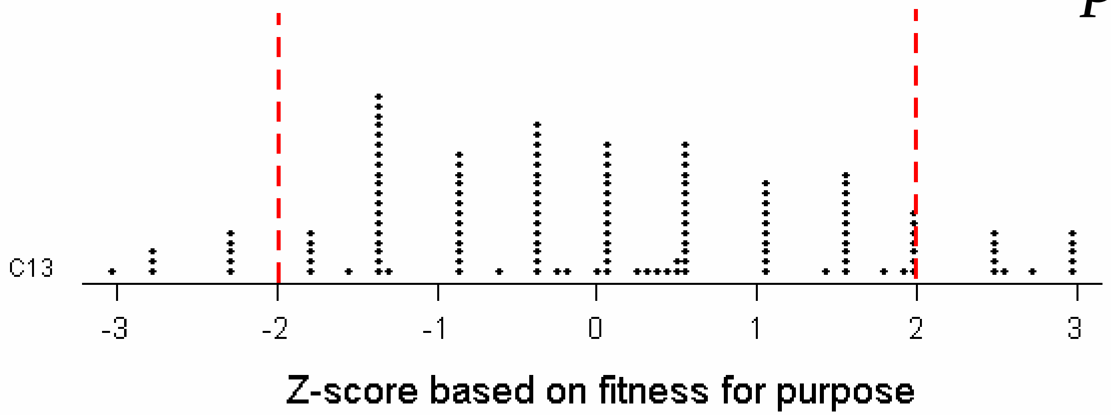
- Robustified against extreme values and informative about fitness for purpose.
- The protocol **is not restricted to consensus values**

“Fit-for-purpose” scoring: Example

- Set fitness for purpose criterion at RSD of 1%. This gives:

$$\sigma_p = 0.01 \times 2.1$$

$$= 0.021$$



- About 78% within 0±2
  - ..for THIS data set with THIS criterion

Non-normal distributions

- Non-normal and multimodal distributions most commonly arise when the participants' results come from two or more inconsistent methods.
- Skews can arise as an artefact at low concentrations of analyte as a result of data recording (mal)practice.
- Sometimes skew can arise when the distribution is fundamentally non-normal
  - Example: GMO data expected to be approximately lognormal
  - **Transform before evaluation**

Handling Multimodal data

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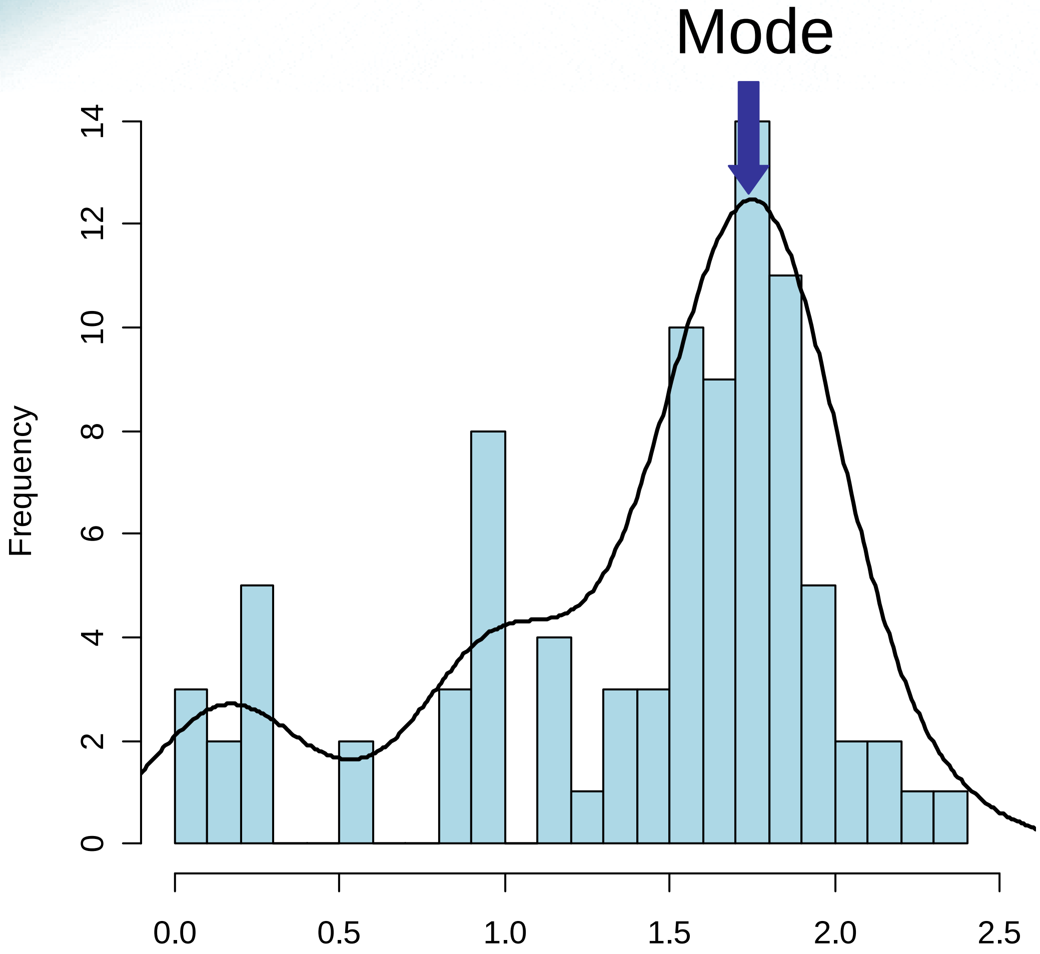

FAPAS Arsenic data, round 0750

- Generate kernel density (h=0.75σ_p)
- Minor modes large
- Largest mode deemed ‘correct’*
- Use Kernel Density Mode

* If not, abandon scoring and investigate further

Uncertainty of the mode

- The uncertainty of the consensus can be estimated as the standard error of the mode by applying the bootstrap to the procedure.
- The bootstrap is a general procedure based on resampling for estimating standard errors of complex statistics.
- Reference: *Bump-hunting for the proficiency tester – searching for multimodality.* P J Lowthian and M Thompson, *Analyst*, 2002,**127**, 1359-1364.

Homogeneity testing in HP1/HP2: Procedure

- Comminute and mix bulk material.
- Split into distribution units.
- Select *m*>10 distribution units at random.
- Homogenise each one.
- Analyse 2 test portions from each in random order, with high precision, and conduct one-way ANOVA on results.

Homogeneity testing in HP1/HP2: Differences

- Rejects if

$$s_{sam} \leq 0.3\sigma_{p}$$

- Forbids outlier rejection

- Uses Thompson-Fearn test for “sufficient homogeneity”
- Requires (1) within-bottle outlier rejection

“Sufficient homogeneity” in HP1

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- Material passes homogeneity test if

$$s_{sam} \leq 0.3\sigma_p$$

- Problems are:
  - s_{sam} may not be well estimated (9 degrees of freedom);
  - single-laboratory precision often close to $0.3\sigma_p$
  - too big a probability of rejecting satisfactory test material.

New protocol: Fearn-Thompson test

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- Test $H_0 : \sigma^2_{sam} < \sigma^2_{all} \;(\text{usually}\,0.3)$

- Reject when

$$s^2_{sam} > \frac{\sigma^2_{all}\chi^2_{m-1}}{m-1} + \frac{s^2_{an}\left(F_{m-1,m} - 1\right)}{2}$$

- Less likely to reject at random

Ref: *Analyst*, 2001, **127**, 1359-1364.

Why use outlier rejection?

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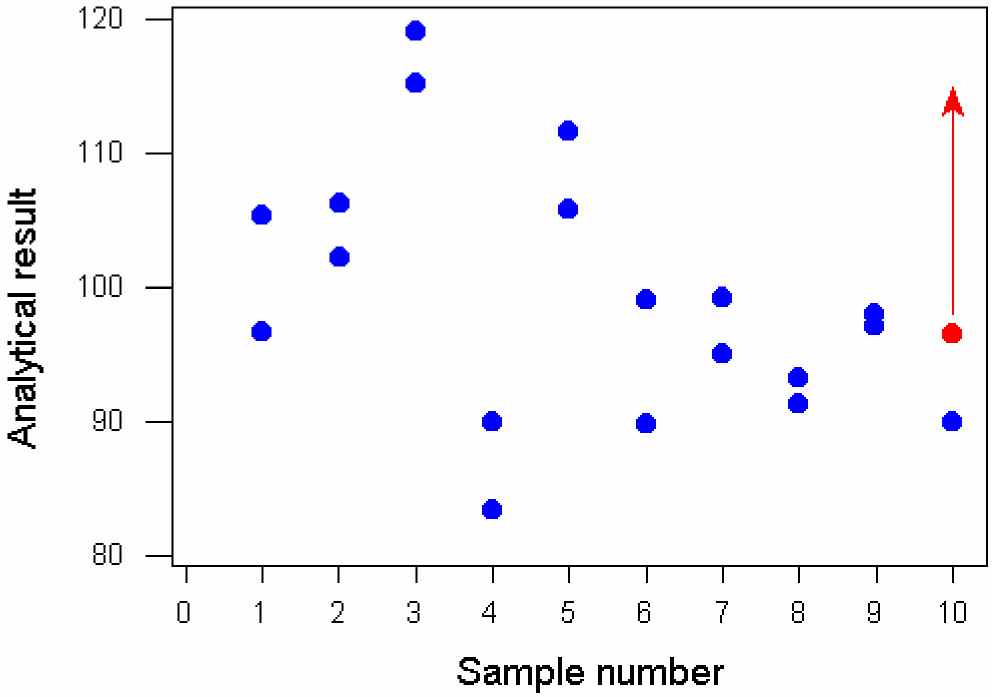
One-way ANOVA gives:
F = 9.5; p = 0.001



Why use outlier rejection?

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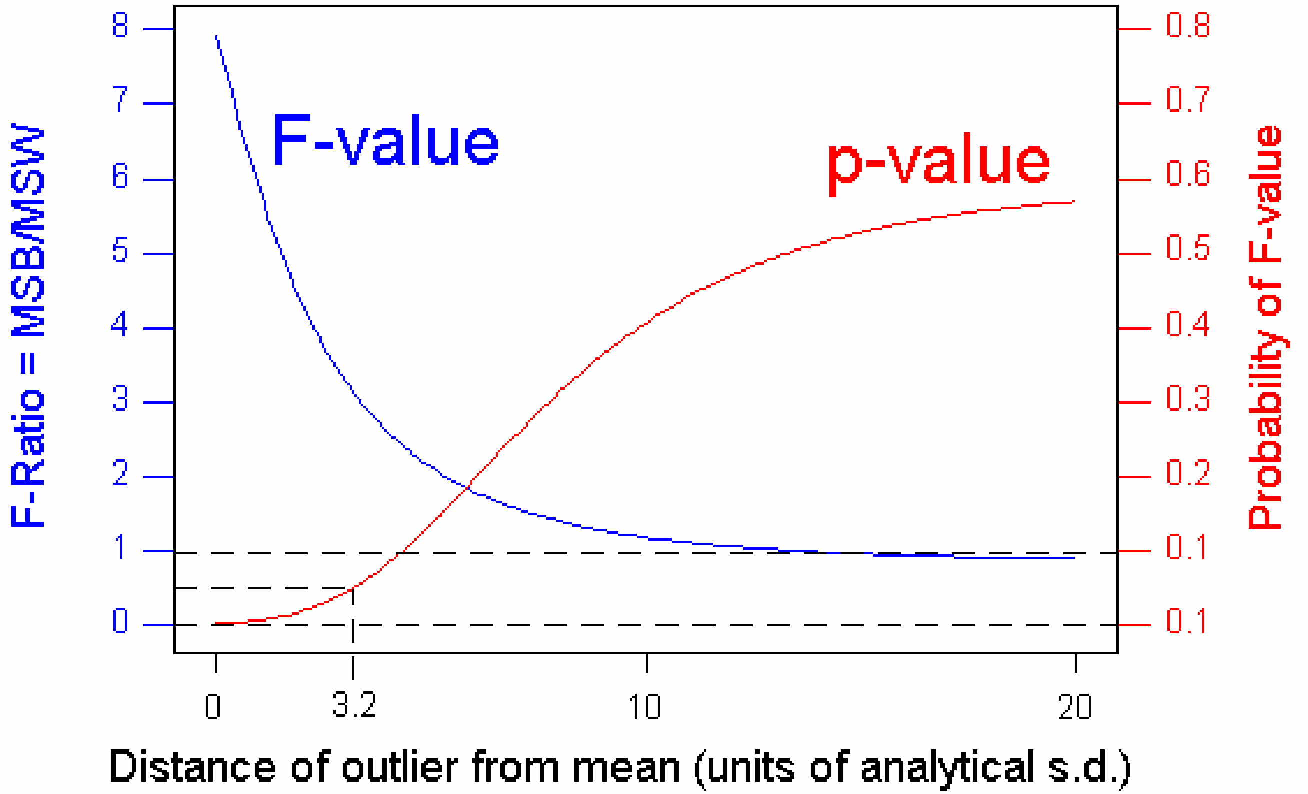

Within-bottle outliers weaken the homogeneity test

Conclusion: New directions in the IUPAC protocol

LGC
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- Stronger emphasis on fitness-for-purpose in scoring
- Clear acceptance of continued use of consensus values
  - with advice on implementation
- Testing for statistical evidence of insufficient homogeneity instead of fixed value
- Does not recommend that the organiser provide scores based on participant uncertainties
  - DOES control uncertainties in assigned value
  - Provides methods for participants to assess their own uncertainty and fitness for purpose