

Horwitz Ratio (HorRat)

as an extended criterion for the assessment of the reproducibility in collaborative trials



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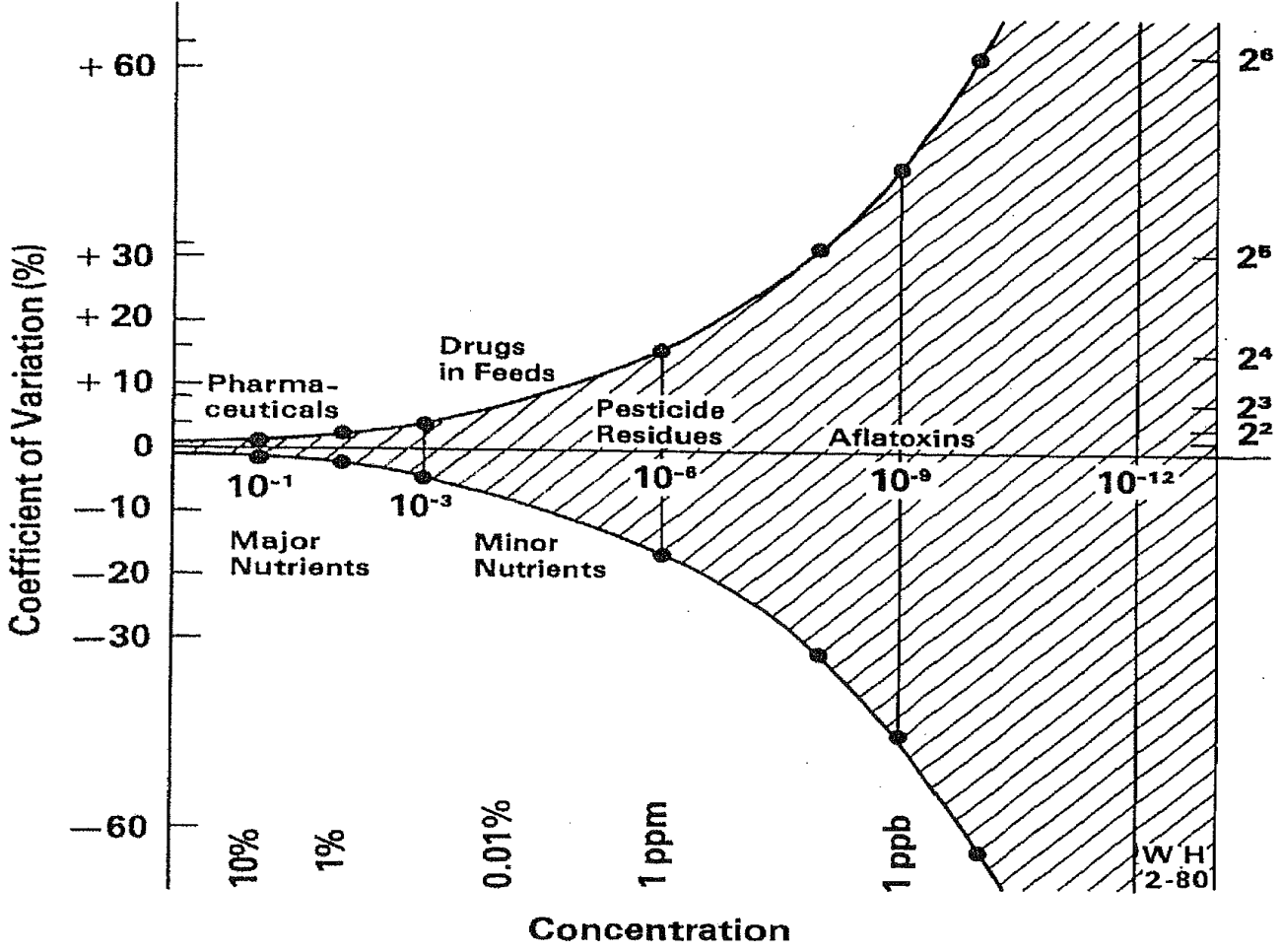
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The Horwitz Equation

- In the 1980's Horwitz et al. published a relationship between the precision of an analytical method and the concentration of the analyte according to the following equation [1]:
 - Predicted $RSD_R = 2^{(1-0.5 \log C)} \%$ (*empirically set*)
 - With RSD_R is the relative standard deviation (= coefficient of variation, CV) under reproducibility conditions (R)
- C is the concentration of the analyte expressed as a dimensionless mass fraction
- Conclusions:
 - The RSD_R appears **only** to be dependent on the concentration and **not** on the nature of the analyte, the test material or the analytical test method/technique
 - The RSD_R increases by a factor of **two** as the concentration of the analyte decreases over two orders of magnitude. So at 100 % concentration of analyte the RSD_R is about 2 %, at 1 % it is about 4 % and at 0.01 % (100 ppm) it is about 8 % (🦄 Horwitz Trumpet)

[1] W. Horwitz, L.R. Kamps, K.W. Boyer, *J. Assoc. Off. Chem.*, **63**, 1344 (1980)

The Horwitz Trumpet



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- Equation:

$$\text{HorRat} = \frac{\text{RSD}_R}{\text{PRSD}_R}$$

- with
RSD_R is the reproducibility obtained from the collaborative trial
PRSD_R is the predicted reproducibility obtained from the Horwitz equation

- Translation:

HorRat < 1: RSD_R of the method is below the predicted value




HorRat = 1: RSD_R of the method is equal to the predicted value

HorRat > 1: RSD_R of the method exceeds the predicted value

HorRat as a benchmark criterion ?

- If HorRat is $\gg 1$, the analytical method is undoubtedly suspect to perform worse than expected/hoped (e.g. due to method deficiencies or due to interferences, contaminations or sample inhomogeneity)
- If HorRat is $\ll 1$, suspect comes out that the collaborative trial was not performed correctly and it gives precision values that are too optimistic (e.g. due to less participants or prior knowledge of analyte content)
- If HorRat is close to 1, method precision in terms of reproducibility is close to the predicted value
- Which HorRat value/range is suitable as a performance benchmark ?

DAPA proposal/recommendation

HorRat value/range	Remark	
$0.3 \leq \text{HorRat} \leq 1$	Fully acceptable Recommended range	
$\text{HorRat} < 0.3$ or $1 < \text{HorRat} \leq 2$	Acceptable but reasonable explanation required !	
$\text{HorRat} > 2$	Not acceptable	

The End.....

Thank you for your kind attention

