

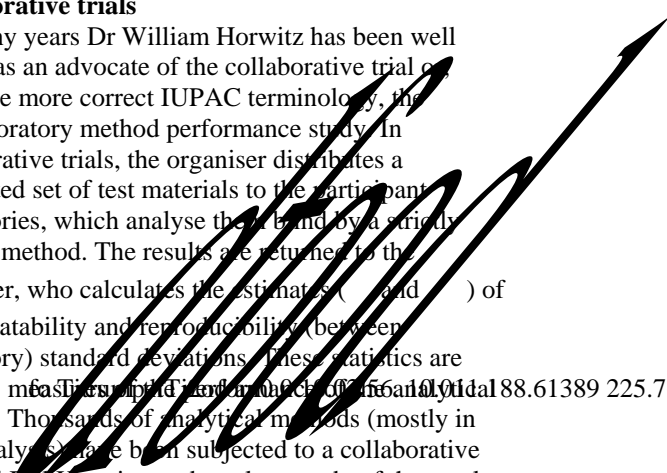
amc technical brief

Editor: M Thompson AMC Technical Brief No.17 July 2004 © Royal Society of Chemistry 2004

The amazing Horwitz function

Collaborative trials

For many years Dr William Horwitz has been well known as an advocate of the collaborative trial or, using the more correct IUPAC terminology, the interlaboratory method performance study. In collaborative trials, the organiser distributes a duplicated set of test materials to the participant laboratories, which analyse them by a strictly defined method. The results are returned to the organiser, who calculates the estimates (s_r and s_R) of the repeatability and reproducibility (between laboratory) standard deviations. These statistics are taken as measures of the random effect of the analytical method. Thousands of analytical methods (mostly in food analysis) have been subjected to a collaborative trial and Bill Horwitz made a close study of the results.



Moreover, the empirical exponent for the region between 10 ppb and 10% m/m is not exactly as given in the Horwitz function but closer to 0.824. But despite these small deviations, the Horwitz function is still impressive, as can be seen in Figure 2.

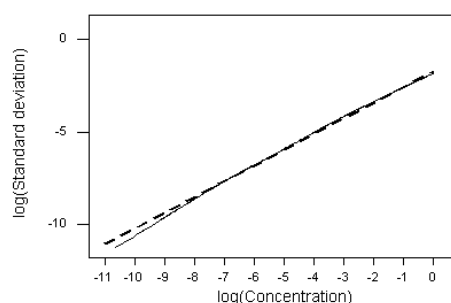


Fig 2. Trend of data from collaborative trials (shown as a lowess fit, solid line) compared with the Horwitz function (dashed line). The systematic deviation below about 10 ppb is apparent. Units are mass fractions (e.g., 1% = 0.01, 1 ppm = 10^{-6} .)

Compilations of data from proficiency tests show similar functions. For example, early data from FAPAS (a foodstuffs proficiency test scheme) gave an excellent fit to a Horwitz-style function³, of the form $\sigma = 0.023c^{0.826}$. This indicates a slightly lower precision than collaborative trials, but that is hardly surprising: proficiency test data include uncertainty due to variation in analytical method, obviously not present in collaborative trials.

A benchmark

The Horwitz function is now widely used as a benchmark for the performance of analytical methods, via a measure called the 'Horrat' which is defined as

$$\text{Horrat} = s_R / \sigma_H$$

An analytical method that during collaborative trial gives Horrats that are substantially worse than unity is regarded as flawed and requi