A natural history of analytical methods†

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It is postulated that, since analytical methods adapt to user requirements by an evolutionary process, the Horwitz function, which predicts reproducibility precision, must be regarded as a fitness-for-purpose criterion in appropriate sectors of analytical chemistry.

Analytical methods once they are devised are, like lifeforms, subject to evolution. Natural selection, here mediated by analytical chemists, ensures that only the fittest analytical methods survive. Methods that provide false information with too high a probability, or true information at too high a price, become extinct, while their modified descendants may survive. We can confidently expect, after many generations and extinctions, that analytical methods will automatically have adapted to their environment. In short, they will approach fitness for purpose (in the sense defined as loss minimisation1). We can even expect that a general pattern of performance will emerge naturally for a whole sector of analysis, just as such patterns emerge for lifeforms. The Horwitz function2 an empirical relationship between reproducibility precision and concentration of the analyte, is just such a manifestation of this evolutionary process.

The Horwitz function, observed in data collected in the analysis of food and drugs, is a remarkable generalisation. Over a wide range of concentration it describes the properties of an analytical method well, apparently without regard to the nature of the analyte or the type of test material, and regardless of the physical principle underlying the analytical method or the complexity of the procedure. It applies equally well to data collected in 1920 or in 1990. It is true (in the sense of unbiased) for analyte concentrations spanning a concentration range from about 5 ppb to 10% m/m, about seven orders of magnitude.

Perhaps most remarkably, the Horwitz function can be expressed simply, although, at first sight, rather oddly: the predicted reproducibility standard deviation is proportional to the concentration of the analyte raised to a power of about 0.85, specifically, $s_H = 0.02c^{0.85}$, when the variables are expressed as mass fractions. At the moment we cannot explain why the function takes this particular form. This type of fractional dimension is, however, seen in many examples from biological evolution. For example, we see it in a plot of brain mass versus body mass in mammals. This too is a manifestation of evolution towards fitness for purpose in the mammalian class.

The nature of the Horwitz function is clearly not determined by chemistry or physics, but by the use to which the analytical data is being put. Accordingly, we are almost compelled to regard the function as more than a mere description of interlaboratory uncertainty. We may think of it, at least for the present and where similar evolutionary pressures exist, as a general purpose criterion of fitness for purpose.

The Horwitz function seems moderately transportable; for example, although it is derived from data drawn from the food and drugs sector, the function applies rather well to the analysis of rocks. Of course it cannot be universally applicable: there are analytical sectors that demand better reproducibility. An obvious example is in the assaying of precious metals, a more hostile environment than food and drugs in some respects. A less obvious example is in the determination of residues of toxic compounds at sub-ppb concentrations.

Regardless of its current success, we must exercise caution with the Horwitz function in the future. It may represent fitness for purpose now, but purposes change and analytical methods will have to adapt to the new environments. Such evolution may well take place in a more consciously directed manner, for instance, in the context of loss minimisation when the joint costs of sampling uncertainty and analytical uncertainty are considered.

References

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