PD 002

Testing the accuracy of analytical standards used for quantitative determination of pesticide residues

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The accuracy of analytical standard solutions is the primary precondition for obtaining reliable results. The accuracy of the primary standard solutions is rarely tested. Analysts tend to assume that the standard solutions freshly prepared are accurate that is the nominal concentration and the true concentration of the analytes in the standard solutions are practically the same. How long a standard mixture can be stored and used is asked more frequently. The DGSANTE Guidance document postulates, without providing the statistical tests to verify it, that the maximum acceptable deviation from the initial concentration is 10%. One method, which is often used, is to compare the mean responses obtained with repeated analyses the two standard solutions using the two sample t-test. It is based on the null hypothesis (H0) that the two mean responses are equal. If the null hypothesis is retained, the default is to assume that the two means are equal. This test may not be appropriate to demonstrate equivalency between the two solutions since the test is designed to prove that two sets of data have different means, not that the two sets have equivalent means. A statistical test called the two one-side t-test (TOST) is the appropriate one which begins with the opposite null hypothesis, that the two mean values are not equivalent. The TOST test requires the specification the smallest difference ±q in mean values for the two standard solutions that is deemed as practically important. The H0 and the alternative hypothesis H1 are described in terms of the difference in means and q.
H0: m1-m2≤q
H1: qL<m1-m2<qu
The alternative hypothesis is proven at a specified level of confidence when the true difference in means between the methods is within the boundaries specified by ±θ.
The TOST is calculated at 95% confidence level as:

$CI= \bar{x}\_1-\bar{x}\_2 \pm t\_(90,(n\_1+n\_2-2)) \cdot \sqrt{(s\_p\hat{}2\ (1/n\_1+1/n\_2))}$

If the CI is completely contained with the range defined by ±q (10% according to DGSANTE GD) the two standard solutions are considered acceptable.
The method of preparation of standard solutions may significantly affect their accuracy and uncertainty.

We will present with practical examples the application of TOST and illustration of the effect of standard preparation method on our poster.