

HORWITZ EQUATION AS QUALITY BENCHMARK IN ISO/IEC 17025 TESTING LABORATORY

Carlos Rivera¹, Rosario Rodríguez²

Bufete de ingenieros industriales, S.C.

Pimentel 4104 –B; Col. Las Granjas. Chihuahua Chihuahua Mexico. C.P. 31160

¹Carlos@Bii.com.mx, ²Rosario@Bii.com.mx

Abstract

L'équation de Horwitz est l'un des premiers paramètres empiriques à un usage en tant que valeur de référence pour les activités de laboratoires de contrôle qualité et des programmes d'essais d'aptitude. Ce document résume le concept de l'équation de Horwitz, des analyses de ses propriétés; propose d'utiliser l'équation dans des laboratoires qui se conforment à la norme ISO / CEI 17025, et considère l'application des protocoles d'essais d'aptitude. Ce travail met l'accent sur une portée juridique et industrielle métrologiques, la discussion entre la communauté scientifique métrologique est citée pour compléter les limites de l'application.

The Horwitz equation is one of the first empirical parameters with a usage as a reference value for laboratories quality control activities and proficiency testing programs. This paper summarizes the concept of the Horwitz equation; analyzes its properties; proposes using the equation in laboratories that comply to ISO/IEC 17025; and considers the application for proficiency testing protocols. This work emphasizes on a legal and industrial metrological scope; the discussion among the scientific metrological community is cited to complete limitations of the application.

INTRODUCTION

Laboratory accreditation bodies accept S^2_R as the main source of uncertainty on analytical measurements, but the doubt on its fitness for purpose remains when no test against a benchmark is done.

The international standard ISO 5725-2 presents the basic methodology to calculate the repeatability S^2_r and the reproducibility S^2_R ; with those values it is possible to evaluate the homogeneity of the variances through F tests or Chi Square tests. In both cases, the user must decide which reference value σ^2 will be set.

The standard for proficiency testing requirements ISO 17043 [1] clause B.3.1.3 subsection c) names the calculation of standard deviation for proficiency assessment as δ under the following situations:

- a fitness for purpose goal for performance, as determined by expert judgment or regulatory mandate (prescribed value);
- an estimate from previous rounds of proficiency testing or expectations based on experience (by perception);

- an estimate from statistical model (general model);
- the results of a precision experiment; or
- participant results, i.e. a traditional or robust standard deviation based on participant results.

The international standard for proficiency testing by interlaboratory comparisons ISO 13528 [2] clause 7.4.2 quotes Horwitz equation without any comments regarding its scope.

The previous statements question common subjects: Which value is good enough to express S^2_R ? If there is a lack of information in some analytical methods, which benchmark may be used? Does the selected benchmark suit as reference? Most of the times metrologists have general ideas to answer the latter, even though an accepted reference is required.

The context. The works to establish general rules for evaluating and expressing uncertainty in measurement started in 1977. The new parameter emerges from the Recommendation 1 (CI-1981) of the Comité International des Poids et Mesures (CIPM) and the Recommendation INC-1 (1980) of the Working Group on the Statement of Uncertainties. [3].

Also in 1977 during the “Annual University of Wisconsin Conference on Analysis”, a team of analytical chemists presented their findings on quality control concluding that the variance on instrumental methods was a function of the concentration, instead of an analytical system’s modernity [4]. Today, the function is known as the Horwitz equation.

It is remarkable to find out that while the scientific metrology sought for general rules on the expression of variance, the analytical chemistry found its own equation for the variance.

Methods - Endorsing Organizations. In 2006 Horwitz and Albert wrote that the Horwitz equation has been used as a reference for the interlaboratory precision. Among the organizations cited in their paper are the International Union of Pure and Applied Chemistry (IUPAC, 1990); Nordic Analytical Committee (NMKL, 1996); International Commission for Uniform Methods of Sugar Analysis (ICUMSA, 2004) and the European Committee for Standardization (CEN, 2004). It is important to mention that authorities of the European Union have included the Horwitz equation as an acceptance criteria [4].

Uncertainty applications. The documents published in 2009 by the Australian accreditation body National Association of Testing Authorities (NATA) [5], and the Codex Alimentarius Commission [6] recognize the Horwitz equation as a source of variance on analytical methods and accept the expression of uncertainty by its values.

THE HORWITZ EQUATION

In 1980 Horwitz, Kamps, and Boyer pointed out that: “an examination of the results of over 50 interlaboratory collaborative studies conducted by AOAC on various commodities for numerous analytes shows a relationship between the mean coefficient of variation (CV), expressed as powers of 2, with the mean concentration measured, expressed as powers of 10, independent of the determinative method” [7]. Such statement was originally expressed in the form presented by the statistician Jung-Keun Lee as:

$$RSD_R, \% = 2^{(1 - 0.5 \log C)} \quad (1)$$

Where C, is the concentration of analyte expressed as dimensionless mass fraction (numerator and denominator have the same units); and RSD_R is the coefficient of variation CV under reproducibility conditions.

In 1999 Michael Thompson transformed equation (1) into the equivalent form:

$$RSD_R, \% = 2 C^{-0.15} \quad (2)$$

or as a standard deviation:

$$S_R = 2 C^{0.85} \quad (3)$$

The graphical representation of the equation (1) is the curve of the figure 1, it is also known as the Horwitz Horn and was considered as “one of the most intriguing relationships in modern analytical chemistry” [4]. The table 1 shows RSD calculated from equation (1) with different concentrations of analyte which are marked as points on the curve in figure 1.

| Analyte concentration | RSD_R |
|-----------------------|---------|
| 10 % | 2.8% |
| 1 % | 4.0% |
| 0.1 % | 5.7% |
| 0.01 % | 8.0% |
| 1 Ppm | 16% |
| 1 Ppb | 45% |
| 0.1 Ppb | 64% |

Table 1. Values of Horwitz equation at different concentrations

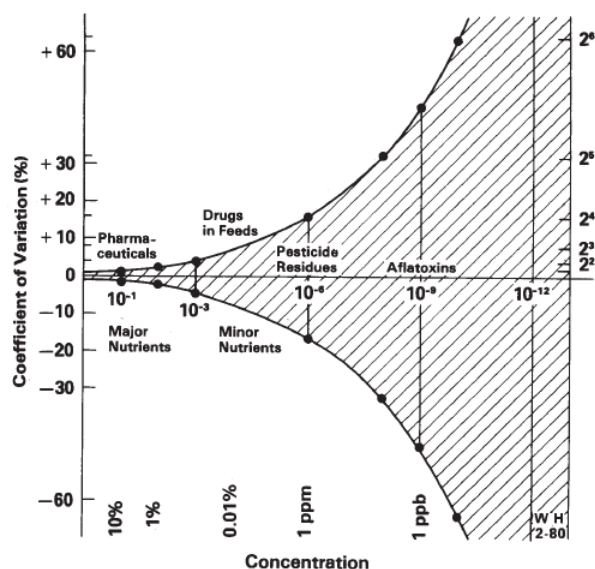


Figure 1. Horwitz Horn, the original curve

Horwitz Ratio (HorRat)

HorRat value [4] is the ratio of the RSD_R calculated from the data of the laboratory, to the RSD predicted from the Horwitz equation presented as $PRSD_R$, thus:

$$HorRat = \frac{RSD_R}{PRSD_R} \quad (4)$$

Under reproducibility conditions, accepted values are between 0.5 and 2.

$HorRat(r)^1$ is a variation to be used on single-laboratory validation studies [8]; its value is the ratio of the RSD_r , in percent, calculated from the data under repeatability conditions, to the RSD predicted from the Horwitz equation, $PRSD_R$, thus:

$$HorRat(r) = \frac{RSD_r}{PRSD_R} \quad (5)$$

Under repeatability conditions, accepted values are between 0.3 and 1.3

Interpreting values of HorRat. AOAC’s supplement [8] explains that values at extremes of the limits of acceptance must be interpreted with caution. With a series of low values of HorRat, check for unreported averaging or prior knowledge of the analyte content; with a series of high values of HorRat, check for method deficiencies such as unrestricted times, temperatures, masses, volumes and concentrations; unrecognized impurities (detergent residues on glassware, peroxides in ether); incomplete extractions and transfers and uncontrolled parameters in specific instrumental techniques.

¹ AOAC considers that within-laboratory acceptance predicted target values for repeatability are given at $\frac{1}{2}$ of $PRSD_R$, which represents the best case.

Limitations on methods

The application of the Horwitz Equation is limited to analytical methods that express measurands as concentration of mass; it does not apply to empirical analytes, indefinite analytes or physical properties, table 2 shows examples of excluded methods. [4]

| Method dependent | Indefinite analytes | Physical properties |
|--------------------------|-------------------------------------|---|
| Moisture Ash Fiber | Enzymes Polymers Biomolecules | Color Density Viscosity Drained weight |

Table 2. Methods excluded from the application of the Horwitz Equation

Limitations on concentrations

Since 1977 further investigations were done regarding properties of the Horwitz Equation, by 1993 Horwitz et al. pointed out that as the concentration decreases and the detection limit is approached (at about 10 ppb), the number of false negatives increases.

Later, in 2000, Michael Thompson found that precision was overestimated at the extremes of the curve presented in figure 1; as a result, the Horwitz Equation was adjusted to the following mathematical model:

$$\begin{aligned} \sigma_R &= 0.22C && \text{if } C < 1.2 \times 10^{-7} \\ \sigma_R &= 0.02C^{0.8495} && \text{if } 1.2 \times 10^{-7} \leq C \leq 0.138 \\ \sigma_R &= 0.01C^{0.5} && \text{if } C > 0.138 \end{aligned} \quad (6)$$

In 2006 Horwitz and Albert pointed out that the adjustment of the model (6) was based just on mycotoxin studies but their conclusions were extended to other analytes and adopted by EU Directives without experimental confirmation [4]. However, nowadays, the model (6) is widely accepted as a valid application, figure 2 shows its shape.

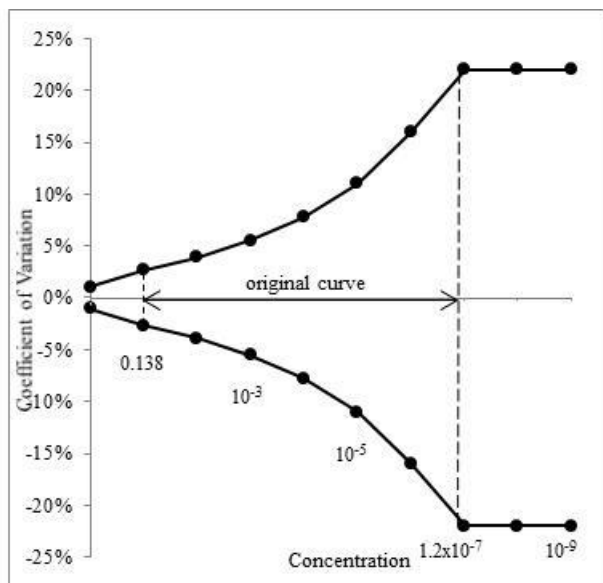


Figure 2. The Horwitz Curve, adjusted

THE HORWITZ EQUATION AND THE LABORATORY ACCREDITATION PROCESS

Laboratories complying to ISO/IEC 17025 must meet metrological requirements for accreditation purposes. The Horwitz Equation may be selected as statistical tool with metrological properties under the following criteria.

Metrological approach

Statistical properties. The Horwitz Equation represents the variance of the reproducibility because the measurement conditions include all the different locations, operators and measuring systems; under the scope of ISO 5725-2 [9] this variance is known as the repeatability of a method of measurement. Under these studies, measurands are the average of different laboratories that work on samples from the same source, this scheme fits the Central Limit Theorem; linking the Horwitz variance with the Gaussian distribution.

The Horwitz Equation was based on the examination of data from about 100 materials examined by multiple laboratories in interlaboratory studies [4]. The size of the sample is big enough ($n > 30$) con consider that the sample variance S^2 behaves like the population variance σ^2 ; then the Horwitz Variance can be defined as the population variance σ^2_H .

Experimental conditions. Figure 3 shows the typical arrangement for interlaboratories study; where the circle represents a homogenous and stable sample distributed – in this case– among three different laboratories, presented as rectangles; each laboratory develops five repetitions, presented as vertical lines.

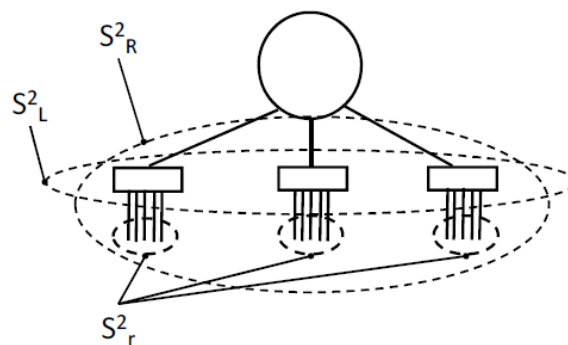


Figure 3. Design for reproducibility study.

In this design three variances of repeatability are known, one of each laboratory; these values are used on ISO 5725-2 to calculate one variance of repeatability S^2_r that represents the variance of the method under repeatability conditions, it is located on the base of the figure.

Moving upward on the design, three means are calculated, one at each laboratory; these values are used on ISO 5725-2 to calculate the variance between laboratories S^2_L ; this estimator is developed under reproducibility conditions, and is located in the middle of the figure 3.

The variance of the whole study is:

$$S^2_R = S^2_L + S^2_r \quad (7)$$

The equation (7) represents the variance of repeatability S^2_R ; if the scope of the study considers changes such as different measurement systems that include changes on laboratories, personnel, equipment or geographic locations; so S^2_R can be characterized as the 'variance of the method' also known as 'the reproducibility of the method'.

On the other hand, the scheme shown in figure 3 can be used to study intralaboratory reproducibility for the same method, considering –in this example– that each rectangle represents a chemist and that the measurement systems are equal. The variances are calculated with the same algorithm, so S^2_R might be identified as the 'variance of reproducibility of the laboratory with changes on chemists' or simply as the 'reproducibility of the laboratory'.

Relations among variances. On experimental arrangements the following conditions are observed (1) the more changes on the conditions of measurement, the bigger the variance will be, so a) the variance of a method might be equal or higher than the variance of the laboratory, b) the reproducibility might be equal or higher than the repeatability; (2) the middle variance S^2_L might be zero or higher. These relations are shown as identities (8.1), (8.2) and (8.3)

$$S^2_R \geq S^2_r \quad (8.1)$$

$$S^2_R \geq S^2_L \quad (8.2)$$

$$S^2_L \geq 0 \quad (8.3)$$

Considering that the Horwitz equation represents the variance of reproducibility, under a wide variations for analytical methods, is reasonable to express:

$$\sigma^2_H = \sigma^2_R \geq S^2_R \geq S^2_r \quad (9)$$

From equation (9) σ^2_H can be named 'the variance of analytical methods', but in this case S^2_L and S^2_r are unknown.

Testing the Variances

The source of the reproducibility studies is fixed on the sample² plus the method³, these elements become the origin of the experiment; so it is reasonable to expect results free of significant differences because the assumption of homogeneity of variances (homoscedasticity) when they come from the same population [10]; as a consequence σ^2_H is a valid reference to evaluate proficiency of analytical methods.

² Homogeneous and stable sample is required.

³ Well known method and explicit measurand should be defined in the protocol of these studies.

Example 1⁴. A laboratory designs the intralaboratory study of reproducibility using a method to quantify concentration of calcium in soil through extraction with ammonium acetate and quantification by ICP; the study is developed by 6 chemists, performing 3 repetitions of the whole process (extraction and quantification). The results are shown in table 2, where the mean and S^2_R were calculated according to ISO 5725-2.

| Units: mg/kg | | | | | | |
|--------------|-------|-------|-------|------------|-------|-------|
| Chemist | 1 | 2 | 3 | 4 | 5 | 6 |
| Average | 4931 | 4907 | 5012 | 4820 | 4749 | 4999 |
| S_i | 194.4 | 232.6 | 120.9 | 172.7 | 152.4 | 129.6 |
| ν | 17 | | | | | |
| Mean | 4903 | | | | | |
| S^2_R | 17009 | | | S_R | 130.4 | |
| σ^2_H | 47664 | | | σ_H | 218.3 | |

Table 2. Data

F test. This tool tests homogeneity of variances [10] checking a proper relationship between them avoiding bias when one is significantly lower than the other. The hypotheses are as follows:

H_0 : If $F_{calc} > F_{tab}$, there is significant difference between variances, so they are not homogeneous.

H_1 : If $F_{calc} \leq F_{tab}$, there is no significant difference between variances, so they are homogeneous.

$F_{calc} = S^2_M/S^2_m$, where S^2_M is the variance with the higher value and S^2_m is the variance with the lower value. The tabulated value of F is for 1-tailed distribution and, 95% confidence level, $\nu = 17$ for experiment data and $\nu > 100$ for reference data. Since experiment was done within laboratory, reference variance will be adjusted as follows⁵:

$$\sigma_H' = \frac{1}{2} \cdot \sigma_H \quad (10)$$

The calculated values are shown in table 3.

| |
|---------------------------|
| $\sigma_H' = 109.2$ mg/kg |
| $F_{calc} = 1.43$ |
| $F_{tab} \approx 1.99$ |
| $H_0 = \text{false}$ |

Table 3. Values for F test.

Therefore, the method is reproducible considering the Horwitz variance as the reference variance.

Discussion. If the reference variance is not adjusted to fit the scope of the study, bias will be induced to the test because $F_{calc} = 2.80$ and $F_{tab} \approx 1.67$; concluding that $H_0 = \text{true}$.

HorRat (r) test. This test works similar to F-test because it evaluates homogeneity of variances through the coefficient of variation –in percentage– and sets upper and lower limits. Hypotheses are as follows:

⁴ Data from this example adjusted to fit the purpose of this paper.

⁵ Criteria come from AOAC, cited in the HorRat (r) section.

H_0 : If $\text{HorRat}(r) < 0.3 \cap \text{HorRat}(r) > 1.3$, there is a significant difference between the coefficients of variation, so variances are not homogenous.

H_1 : If $0.3 \leq \text{HorRat}(r) \leq 1.3$, there is no significant difference between the coefficients of variation, so variances are homogenous. The calculated values are shown in Table 4.

| | |
|--------------------|---------|
| RSD_r | = 2.7 % |
| PRSD_R | = 4.5% |
| $\text{HorRat}(r)$ | = 0.6 |
| H_0 | = false |

Table 4. Values from HorRat (r) test

Therefore, the method is reproducible considering the Horwitz coefficient of variation as the reference variance.

Chi square test. This tool tests the relationship between an observed variance and a reference variance [11]; nevertheless, calculations might be biased because the test only considers the upper limit of acceptance, opening the possibility to inappropriate references. Hypotheses are as follows:

H_0 : If $C_{\text{calc}} > C_{\text{tab}}$, there is significant difference between variances.

H_1 : If $C_{\text{calc}} \leq C_{\text{tab}}$, there is no significant difference between variances.

$$C_{\text{tab}} = 1/\nu \cdot \chi^2_{(\alpha;\nu)} \quad (11)$$

$C_{\text{calc}} = S^2_R / \sigma^2_R$, The tabulated value $\chi^2_{(\alpha;\nu)}$ is for 1-tailed distribution and 95% confidence level; $\nu = 17$ for experiment data. The calculated values are shown in Table 5.

| | |
|-------------------|---------|
| C_{calc} | = 1.43 |
| C_{tab} | = 1.62 |
| H_0 | = false |

Table 5. Values for Chi square test

Therefore, the method is reproducible considering the Horwitz variance as the variance reference.

Proficiency testing

The main difference between proficiency testing and interlaboratory study is that first one produce an output of acceptable / unacceptable results for each participant demanding use of well-known parameter of qualification.

Proficiency tests designed under ISO/IEC 17043 are supported on statistical tools described in ISO 13528 that quotes Horwitz Equation but it does not explain its usage.

Example 2⁶. Three laboratories {A, B, C} participate in a proficiency test that requires determination of the

⁶ Data from this example was adjusted to fit the purpose of this paper.

concentration of pesticide in sample of pear puree with assigned value of 8.9 mg/kg. Each laboratory must process twice the full process with 24 h of difference. Laboratories should use QuEChERS extraction and gas chromatography.

This study has two goals: first evaluate process reproducibility, second evaluate results reproducibility; both cases Horwitz Equation will be used as estimator of the limits.

Results reported by each laboratory are shown in table 6.

| Laboratory | Result 1, mg/kg | Result 2, mg/kg |
|------------|-----------------|-----------------|
| A | 9.2 | 11.4 |
| B | 9.8 | 12.5 |
| C | 5.3 | 9.1 |

Table 6. Results of proficiency test

Evaluation by ranges. This tool is based on subclause 5.2.2.1 in ISO 5725-6 [12], equation (12) defines the critical range, CR, to evaluate results obtained on reproducibility conditions:

$$\text{CR}_{0.95}(n) = f(n) \sigma_R \quad (12)$$

where $f(n)$ is the factor to expand σ_R under n repetitions with 95% confidence level. Laboratories are tested under hypotheses that follow:

H_0 : If $C_L \geq \text{CR}_{0.95}$, there are not reproducibility conditions for the process, so it is unacceptable.

H_1 : If $C_L < \text{CR}_{0.95}$, there are reproducibility conditions for the process, so it is acceptable.

C_L is the statistical range calculated from each laboratory and is calculated by equation that follows:

$$C_L = \text{Higher value} - \text{Lower value} \quad (13)$$

As it is known from table 6, each laboratory did two repetitions, so $n = 2$ thus $f(2) = 2.8$ and $S_R = S_H$ for each laboratory. Results are shown in table 7.

| Units: mg/kg | | | | | | |
|--------------|------|-------|--------------------|-------|-------|--------------|
| lab | Mean | S_H | $\text{CR}_{0.95}$ | C_L | H_0 | Evaluation |
| A | 10.3 | 1.2 | 3.2 | 2.2 | FALSE | Acceptable |
| B | 11.2 | 1.2 | 3.5 | 2.6 | FALSE | Acceptable |
| C | 7.2 | 0.86 | 2.4 | 3.8 | TRUE | Unacceptable |

Table 7. Results of proficiency test

Therefore, accepted laboratories have reproducible analytical processes independently of their bias.

Evaluation of bias. This tool is based on subclause 4.7.2 in ISO 5725-4 [11], equation (13) defines bias, eb, in function of the uncertainty,

$$\text{eb} = \frac{|x - \mu|}{U} \quad (13)$$

where x is the mean of the results from the laboratory, μ is the reference value, U is the uncertainty of the method. Laboratories are tested under hypotheses that follow:

H_0 : If $eb \geq 1$, reported value is biased, so it is unacceptable.

H_1 : If $eb < 1$, reported value is unbiased, so it is acceptable.

For this example $U = \sigma_H \cdot 2$ (this criteria will be discussed in the next section) resulting $U = 2.05$ mg/kg. Summary of this evaluation is shown in table 8.

| Laboratory | eb | H_0 | Evaluation |
|------------|-----|-------|--------------|
| A | 0.7 | FALSE | Acceptable |
| B | 1.1 | TRUE | Unacceptable |
| C | 0.8 | FALSE | Acceptable |

Table 8. Summary of bias evaluation

Therefore, accepted laboratories have reproducible results independently of their precision.

Conclusion. This section shows in brief how Horwitz Equation can be used as known parameter of evaluation in proficiency tests; systematic and random error can be followed by laboratories under this scope. Even though there are other statistical tools that can be used to track similar goals.

Expression of Uncertainty

Section 4.3 in the Guide to the Expression of Uncertainty in Measurement (GUM) [3] describes type B evaluation of standard uncertainty, considerations in subclause 4.3.1 allows inclusion of Horwitz variance as ‘standard uncertainty of the method’. As well GUM does not fix the level of confidence, clause 6.3.3 says: “... is often adequate in measurement situation where the probability distribution characterized by ‘y’ and $u_c(y)$ is approximately normal and the effective degrees of freedom of $u_c(y)$ are of significant size. When this is the case, which frequently occurs in practice, one can assume that taking $k=2$ produces an interval having a level of confidence of approximately 95 percent...” which is the one required by the International Laboratory Accreditation Cooperation (ILAC) to its members [13].

In addition, the Horwitz equation fits the ILAC’s criteria to implementing the equation of Horwitz as the expression of uncertainty [14], considering: 1) the basis for the estimation of uncertainty of measurement is to use existing knowledge. Existing experimental data should be used, 2) if a standard gives a typical uncertainty of measurement for tests results, laboratories are allowed to quote this figure if they can demonstrate full compliance with the test method, 3) the required depth of uncertainty estimations may be different in different technical fields. Factors to be taken into account include: common sense, classification of the degree of rigor in the determination of uncertainty of measurement.

In line with the previous arguments, the uncertainty of measurement for analytical methods, with a confidence level of 95 percent, can be expressed by the equation (14):

$$U_{\text{analytical method}} = \sigma_H \cdot 2 \quad (14)$$

Connecting the dots: application in ISO/IEC 17025 testing laboratories

Laboratories complying to ISO/IEC 17025 [15] are required –under clause 5.4.2– to confirm performance of standardized methods before introducing the tests. In this case, σ_H can be used as reference to evaluate repeatability, reproducibility and bias, as was shown before.

Estimation of uncertainty is required under clause 5.4.6 For this matter, laboratories performing analytical methods with no special requirements (i.e. high accuracy) can adopt $U_{\text{analytical method}}$ as shown in equation (14). NATA and The Codex Alimentarius Commission have published guidance on this issue.

Assurance of the quality of test results is required under clause 5.9; previous examples shown how to use them as recurrent quality controls, introducing the Horwitz Equation as benchmark of the performance. Proficiency tests are required under this clause too.

The Horwitz equation can be used by internal auditors – clause 4.14– to evaluate if precision records show reasonable performance.

Evaluating the application. The Horwitz equation in ISO/IEC 17025 testing laboratories should fit the purpose of intended use; Table 9 proposes a checklist to be fulfilled before its implementation. If any of the answers is “no”, application is not convenient.

| Questions |
|--|
| <input type="checkbox"/> Is a standardized method? |
| <input type="checkbox"/> Is the concentration of analyte expressed as a dimensionless mass fraction? |
| <input type="checkbox"/> Is the method out of the limitations list? |
| <input type="checkbox"/> Is the measurand used under legal or industrial scope? |
| <input type="checkbox"/> Is the Horwitz Variance at last 1/6 of the tolerance of the product under evaluation? |
| <input type="checkbox"/> Do authorities’ criteria allow its application? |

Table 9. Checklist to implement Horwitz equation.

Discussion

Some of the above sections included focused discussions on the application of the Horwitz Equation. Concerns of scientific metrologists regarding application of Horwitz equation as uncertainty expression are pointed out in publications by Lisinger and Josephs ‘Limitations of the Application of the Horwitz equation’ [16]. The inference of ‘scientific metrologists’ comes from their profiles; Lisinger as scientific of reference materials, and Josephs

as scientific of the Bureau Internationale des Poids et Mesures, BIPM. The highlights of their exposition are:

1. When observed values were evaluated against forecasted ones by linear regression, Horwitz equation loses accuracy when concentrations are lower than 5.4 ppm
2. Effects of the matrix of the sample and different methods are not included.
3. Improvements on precision of analytical methods over the time are not included.
4. Even though GUM allows Horwitz equation under “expert judgment”, it requires that measurand and measurement should be known in detail; so application is incorrect.

Thompson answered writing “Limitations of the Application of the Horwitz equation: A rebuttal” [17], his answers are:

1. Linear regression is not the best way to deal with the kind of data used to develop Horwitz equation, besides independent variable is redundant to the regression analysis. The interval that Linsinger and Josephs marked was previously known.
2. To make judgments on applications knowledge of previous usage is required, i.e. Horwitz equation have been complete validated by food-analysis sector; otherwise, the model was adjusted on the extremes of the curve.
3. Application shows behavior of “the worst acceptable precision” because it includes systematic errors of analytical processes; besides if any laboratory is required to improve performance, it is not forbidden.
4. Usage as uncertainty estimator is justified for sectors with proper validation of the application. Is common that industry prefers less accurate, less expensive methods when it is allowed.

Conclusion

Application of the Horwitz Equation is a valuable quality control tool for laboratories operating under industrial and legal metrology; scientific laboratories might find it irrelevant for their purposes. Nevertheless, application must be guided by the critical sense of metrologists.

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