TECHNICAL REPORT

ISO TR 9474

First edition
1993-08-15

Rubber and rubber products — Determination of accuracy and bias of chemical test methods

Caoutchouc et produits en caoutchouc — Détermination de la justesse et du biais des méthodes d'essai chimiques

Reference number
ISO/TR 9474:1993(E)

Contents

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The main task of technical committees is to prepare International Standards, but in exceptional circumstances a technical committee may propose the publication of a Technical Report of one of the following types:

— type 1, when the required support cannot be obtained for the publication of an International Standard, despite repeated efforts;

— type 2, when the subject is still under technical development or where for any other reason there is the future but not immediate possibility of an agreement on an International Standard;

— type 3, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example).

Technical Reports of types 1 and 2 are subject to review within three years of publication, to decide whether they can be transformed into International Standards. Technical Reports of type 3 do not necessarily have to be reviewed until the data they provide are considered to be no longer valid or useful.

ISO/TR 9474, which is a Technical Report of type 3, was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

The reasons which led to the decision to publish this document in the form of a type 3 Technical Report are explained in the introduction.

Introduction

Evaluation of test methods and the quality control monitoring of equipment and operating procedures is carried out by evaluating the precision of the test methods. In chemical test procedures it is essential that a careful assessment of both accuracy and precision is made. In physical and technological test procedures, on the other hand it is frequently only possible to assess the precision of the measurements.

ISO/TR 9272 addresses the assessment of precision which is important for both physical and chemical test methods. The present document addresses both accuracy and bias, vitally important for chemical analyses and also other tests where a 'true' or reference value can be established within ISO/TC45.

This document has been published as a Technical Report to make it more readily available to all who require it for background information in the determination of accuracy and bias in ISO/TC45 chemical test methods.

Rubber and rubber products — Determination of accuracy and bias of chemical test methods

1. Scope

This Technical Report presents guidelines for evaluating the accuracy and bias of ISO/TC45 test method results. These guidelines are additional to those in ISO 5725 and ISO/TR 9272, and give the format for expressing accuracy and bias.

This Technical Report is devoted to test method accuracy assessment and is limited to test method standards that

- have test results expressed in terms of a quantitative continuous variable
- have test results which are quantifiable in absolute terms

The accuracy and bias expression as determined by interlaboratory tests, enable the following to be assessed:

a) the adequacy of the test method submitted to interlaboratory testing, where adequacy refers to the accuracy of the method and low values fixed bias, B_F and relative bias, B_R ;

b) operator bias;

c) sample bias.

2. References

ISO 5725 - Precision of test methods - Determination of repeatability and reproducibility by interlaboratory tests.
ISO/TR 9272 - Rubber and rubber products - Determination of precision for test method standards.
ISO Standards Handbook 3:1989, Statistical methods. (This handbook contains the following International Standards: ISO 2602, ISO 2854, ISO 2859-1, ISO 2859-2, ISO 3207, ISO 3301, ISO 3494, ISO 3534, ISO 3534-3, ISO 3951, ISO 5725.)

3. Definitions

For the purposes of this Technical report, the following definitions apply.

Note 1 -
Definitions of repeatability and reproducibility are given in ISO 5725, with clarification in ISO/TR 9272. Precision is defined in ISO 3534. It is a testing or measurement concept that expresses the ability to generate test results that agree with each other. The type of agreement is normally measured inversely by the standard deviation, high precision corresponding to a low (small) standard deviation. High precision may exist simultaneously with a large bias or poor accuracy.

3.1 true value (see ISO 3534:1977 2.82): An accepted reference value or ideal value for a property, which can be measured experimentally only if all sources of measurement error are eliminated.

Note 2 - In practice a standard reference sample is frequently used. Rubber having zero or another accurately known content of a particular compound or element, is often available or can be prepared.

3.2 accuracy (A): A concept which describes the degree of correspondence between an averaged measured value and the true value or an accepted reference or standard value for the material or phenomenon involved in the test.

Note 3 - The reference or standard value may be established by theory, by reference to an accepted standard, by reference to another test method or by preparation of a known sample.

3.3 bias (B): The difference between the average measured test result and the true value or accepted reference value; bias can be "fixed" or "relative", and both forms may coexist.

Note 4 - High accuracy implies a small or negligible bias, and when bias exists, increased testing does not increase accuracy but merely enhances precision. A graphical representation of various types of bias is given in Annex A. If we think of the accuracy, A in terms of *100% accurate = perfect*, ie. no error of testing, then

$$A = (1 - [V_T - T_R] / V_T) 100$$

where V_T is the true value; T_R is the test result; $[V_T - V_R]$ is an absolute value, regardless of sign. The nearer to 100 the result, the better the accuracy. Bias may be due to a number of factors, but in chemical analysis it is commonly due to the presence of other, interfering chemicals in the sample. Such a chemical may itself give a response in the test, in which case it gives rise to a fixed bias, or it may depress or enhance the response of the chemical sought, therefore acting as a variable bias. The degree of bias will normally vary with the level of the interfering chemical.

3.3.1 fixed bias (B_F): Bias is "fixed" when its value is independent of the level or mean value of the property being measured.

3.3.2 relative bias (B_R) : Bias is "relative" when its value varies with the level or mean value of the property being measured.

3.3.4 composite bias (B_C): composite bias depends on the test result and is quoted as the " composite bias B_C at a specified level of test result".

4. Measurement of Bias

4.1 In the absence of bias, there is a one-to-one correspondence between the mean measured value $\bar{Y}$ and the true value V_T of a parameter, ie.

$$\bar{Y} = V_T \pm \varepsilon \qquad \dots (1)$$

where ε is a random variation component, whose *long run* average is equal to zero. In the presence of a fixed bias, the equation for the measured value becomes

$$\bar{Y}' = V_T + B_F \qquad \dots (2)$$

In the presence of relative bias, the equation for the measured value becomes

$$\bar{Y}'' = a\ V_T \qquad \text{... (3)}$$

where a is the slope of the line in the general equation, $y = a\,x$ and $(a - 1)$ is the bias.
In the simultaneous presence of both a fixed and relative bias, the equation becomes

$$\bar{Y}''' = a\ V_T + B_F \qquad \text{... (4)}$$

The measurement error or "composite bias" is given by

$$\bar{Y}''' - V_T = (a - 1)V_T + B_F = B_C \qquad \text{... (5)}$$

Note 5 - Only those cases where the relation between "measured" and "true" values is linear, are considered in this Technical Report.

4.2 In order to measure bias, it is necessary to have access to both "measured values" and to one or more "true values". Samples with accurately known "true values" may be commercially available or capable of being prepared. Although a "true" value can never be known absolutely, its value frequently can be known to an uncertainty tolerance (or mean deviation) much less (factor of 10) than the precision of the measurement technique being assessed. This is particularly true of chemical analyses, though it is rarely so for 'technological' physical properties.

4.3 Commonly used methods of estimating bias are the following:

a) single standard reference
b) multiple standard reference

These are described in clause 5.

5. Methods for Measurement of Bias

5.1 General - The methods described in this clause are based on the assumption that the distribution of errors is a normal one. This assumption should be verified by appropriate statistical methods.

Note 6 - For many measurement methods, the distribution of errors is not normal and therefore the methods proposed in this clause give only an approximation of the true bias of the system. The reference sample should be a sample having a known concentration of the chemical being sought, and should be in all other significant respects identical to the test sample.

5.2 Single reference sample method

5.2.1 In cases where only one reference sample is available, it is not possible to separate the observed bias into its "fixed" and "relative" components. Only the "composite" bias B_C can be estimated.

5.2.2 Composite bias is given by the expression

$$B_C = \bar{Y} - V_T \qquad \text{... (6)}$$

where $\bar{Y}$ is the mean of n determinations; V_T is the "true" value.

5.2.3 The statistical treatment of composite bias is based on the concept that the bias is a random variable that follows Student's *t* distribution. A *t* value, *t (calc)*, is evaluated from the following equation

$$t\,(calc) = (\bar{Y} - V_T) / [\,S / (n)^{1/2}\,] \qquad \text{... (7)}$$

where *t (calc)* has (n-1) degrees of freedom and where $\bar{Y}$ is the arithmetic mean of n separate measurements, and S is the standard deviation of those n measurements. The usual equation for calculating S is used, see equation 8, where the summation is taken from i = 1 to i = n.

$$S = \{\, 1/(n-1)\ \Sigma (Y_i - \bar{Y})^2 \,\}^{1/2} \qquad \text{... (8)}$$

5.2.4 The next step is to make a statement about the significance of *t (calc)*,ie. is the magnitude of the bias or difference ($Y - V_T$) compared to the variation of the measurements used to calculate Y, significantly different than zero? For this purpose the value of *t (calc)* must be compared to a critical *t*, *t (crit)*, at some selected probability or significance level. The usual probability value is 0.05 which is equivalent to a significance level of 95% ie. when a *t (calc)* value is declared to be significantly greater than zero, the probability that the declaration statement is true is 95% or conversely the probability of the statement being in error is 5% (0.05). Other probability (or significance) levels such as 0.02 or 0.01, corresponding to 98% and 99% significance respectively, may be used if higher significance is desired. The critical value of *t* at the required degrees of freedom, may be obtained from published statistical tables (eg. Physical Testing of Rubber, ed. R. P. Brown, published by Elseivier Applied Science, or other sources).

5.2.5 A non-zero bias is declared if equation 9 is true, where | *t (calc)* | is the absolute value disregarding sign.

$$|\,t\,(calc)\,| > t\,(crit) \qquad \text{... (9)}$$

5.2.6 The confidence interval, CI, for the composite bias ($Y - V_T$), is given by the following equation

$$CI = +/- \ [\, t\,(calc)\, S \,/\, (n)^{1/2}\,] \qquad \text{... (10)}$$

5.2.7 An estimate of the sample size (number of measurements, n) suitable for obtaining the composite bias within a certain tolerance or range of values equal to +/- δ, with a selected significance level as determined in 5.2.4, may be found from

$$n = [\, t\,(crit)\, S \,/\, \delta \,]^2 \qquad \text{... (11)}$$

5.3 Multiple reference sample method

5.3.1 Linear regression techniques are used with multiple reference samples. An example of such use is given in Annex B.

5.3.2 A set of reference samples is selected or prepared. For each of these the component of interest in the material to be analyzed has a different known or true value, (Xt). The values of (Xt) should span the normal range encountered with the test method. On each of these reference samples, one or more (measurements) determinations are made of the component of interest. These average measured (determination) values are designated Yi.

$$Yi = a\ Xi + b \qquad \text{... (12)}$$

(The subscript t on X has been dropped for simplicity.)

5.3.3 Plot the values of Xi and Yi on the X and Y axes. The values of the slope of the regression line, a, and the intercept, b, are determined by the least-squares method. This can be done on an electronic calculator or the " by the hand" method described in Annex C.

5.3.4 An unbiased value of the fixed bias, B_F, is equal to b, and the relative bias, B_R, is equal to (a - 1). The composite bias, B_C, for any particular value of X (not necessarily a measured value) is given by the equation

$$B_C = (a - 1) X + b \quad \text{... (13)}$$

5.3.5 The slope standard error, S (a), is determined using equation

$$S (a) = S_R / (S_{XX})^{1/2} \quad \text{... (14)}$$

where the "standard error of the estimate" (variation of points about regression line), S_R is given by

$$S_R = \{ [S_{YY} - (S^2{}_{XY} / S_{XX})] / \; n - 2 \; \}^{1/2} \quad \text{... (15)}$$

and

$$S_{YY} = \Sigma \; (Yi - \bar{Y})^2 \quad \text{(sum from } n = 1, n = i) \quad \text{... (16)}$$

The terms S_{XX} and $S^2{}_{XY}$ are defined in Annex C.

The intercept b standard error, S (b), is determined using equation

$$S (b) = S_R [(1/ n) + (\bar{X}^2 / S_{xx})]^{1/2} \quad \text{... (17)}$$

Note 7 - The value of S_R may also be expressed in terms of the correlation coefficient (between X and Y) denoted by r_{xy} by way of the following

$$S_R = \{ [S_{YY} / (n - 2)] [1 - (r_{xy})^2] \}^{1/2} \quad \text{... (18)}$$

5.3.6 The confidence *interval* for the relative systematic error (a - 1), corresponding to the determined confidence (significance) probability at (*n* - 2) degrees of freedom as in clause 5.2.4 , may be expressed in the following way

$$(a - 1) - (t \, (crit) \, S (a) ; \quad (a - 1) + (t \, (crit) \, S (a) \quad \text{... (19)}$$

The confidence *interval* for the fixed bias, b , corresponding to the confidence (significance) probability at (*n* - 2) degrees of freedom as in clause 5.2.4, can be expressed as

$$b - t \, (crit) \, S (b) ; \quad b + t \, (crit) \, S (b) \quad \text{... (20)}$$

5.3.7 The sample size n_R , (number of X,Y data pairs) suitable for determining the relative bias (a - 1) to a chosen tolerance (range) of +/- L, for a given confidence (significance) level with *n* -2 degrees of freedom is given by

$$n_R = 2 + \{ (t \, (crit))^2 [S_{YY} \; S_{XX} - (S_{XY})^2] / L^2 \; (S_{XX})^2 \} \quad \text{... (21)}$$