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Rubber and rubber products — Determination of the sensitivity of test methods

*Caoutchouc et produits en caoutchouc — Évaluation de la sensibilité
des méthodes d'essai*



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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 19004 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analyses*.

This International Standard is based on ASTM D 6600-00, *Standard Practice for Evaluating Test Sensitivity for Rubber Test Methods*, copyright ASTM, used with permission of ASTM.

Introduction

Testing is conducted to make technical decisions on materials, processes and products. With the continued growth in the number of test methods available for determining physical and chemical properties of rubber and rubber products, a quantitative approach is needed to select test methods that have high quality or technical merit (or the method which has the highest). The procedures defined in this International Standard may be used for this purpose.

One index of technical merit frequently used in the past for test methods has been the precision of the method. The precision is usually expressed as some multiple of the test measurement standard deviation for a defined test domain. Although precision is a quantity required for test sensitivity, it is an incomplete description (only one-half of the necessary information) since it does not consider the discrimination power (sensitivity) of the method with respect to the property (or constituent) being determined.

Any attempt to determine the relative sensitivity of two different test methods on the basis of measurement standard deviation ratios or variance ratios, which give no information on the discrimination power of the methods, constitutes an invalid quantitative basis for determining the sensitivity. Coefficient of variation ratios (which are normalized with respect to the mean) may constitute a valid way of determining relative sensitivity, but only when the results obtained by the two test methods under comparison are directly proportional or reciprocally related to each other. If the relationship between two test methods is non-linear, or linear with a non-zero intercept, coefficient of variation ratios are not equivalent to the true test sensitivity as defined in this International Standard (see discussion in B.1.4 in Annex B).

This International Standard develops the terminology and concepts required to define and determine the sensitivity of a test method. Sufficient background information is presented to place the standard on a firm conceptual and mathematical foundation. This allows broad application of the standard across both chemical and physical test domains. The standard draws heavily on the approach and techniques given in references [1] and [2] in the Bibliography.

The text starts by giving definitions of a number of general terms and a brief review of the measurement process. This is followed by development of basic test sensitivity concepts. Two classes of test sensitivity (absolute and relative) are defined, as well as two categories:

- a) sensitivity determined over a limited measured-property range (category 1);
- b) sensitivity determined over an extended range (category 2).

For an extended property range, for either class, two types of test sensitivity may exist:

- 1) uniform or equal sensitivity across a range of property values (type 1);
- 2) non-uniform sensitivity, i.e. the sensitivity depends on the value of the property across the selected range (type 2).

Annex A is an important part of this document. It presents recommendations for using linear regression analysis for the determination of test sensitivity and recommendations for determining the precision of the test sensitivity determination.

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Annex B is also an important adjunct to the document. It gives two examples of relative test sensitivity calculations:

- a) for a limited-range or “spot check” programme;
- b) for an extended-range test sensitivity programme in the case of a non-uniform test sensitivity.

Annex C gives background information on transforming the scales of plots, as is often needed for an extended-range sensitivity. It also gives the derivation of the absolute test sensitivity for a simple analytical chemical test.

Rubber and rubber products — Determination of the sensitivity of test methods

1 Scope

This International Standard describes how test sensitivity can be determined for test methods used to measure typical physical and chemical properties of rubber and rubber products. It is also applicable to tests used to measure the properties of carbon black fillers.

Test sensitivity is defined as the ratio of the discrimination power of a test method for the fundamental property to be determined to the measurement error expressed as a standard deviation. It is frequently described as the “signal-to-noise ratio”.

This International Standard does not address the topic of sensitivity in the context of threshold (i.e. minimum) detection limits in the determination of very low or trace constituent levels.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TR 9272, *Rubber and rubber products — Determination of precision for test method standards*

ISO 5725 (All parts), *Accuracy (trueness and precision) of measurement methods and results*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 5725, together with the following, apply.

NOTE A number of specialized terms or definitions, not appearing in other International Standards, are required for this International Standard. They are defined in this clause in a systematic sequential order, from simple terms to complex terms; the simple terms may be used in the definition of the more complex terms. This approach generates the most succinct and unambiguous definitions. Some key concepts required for this International Standard are introduced and defined in other clauses of the standard. Their location in these other clauses puts them in a more appropriate context and makes understanding the concepts easier.

3.1 fundamental property

FP

inherent or basic property (or constituent) that a test method is intended to determine or assess

3.2 measured property

MP

property that a measuring instrument determines

NOTE It is related to the fundamental property by a functional relationship $MP = f \times FP$ that is known or that can be readily determined by experiment.

3.3
reference material
RM

material (or other object) selected to serve as a common standard or benchmark for measured property (MP) measurements for two or more test methods

NOTE The expected measurement value for each of the test methods, designated as the reference value, may be known (from other sources) or it may be unknown.

3.4
calibration material
CM

material (or other object) selected to serve as a standard or benchmark reference material, with a fully documented fundamental property (FP) reference value for a test method

NOTE 1 It (along with several other similar materials with documented FP reference values) may be used to calibrate a particular test method or may be used to determine test sensitivity.

NOTE 2 A fully documented FP reference value implies that an equally documented measured property value may be obtained from an $MP = f \times FP$ relationship. However, unless $f = 1$, the numerical values of the measured property and the fundamental property are not equal for any calibration material.

3.5
test domain

operational conditions under which a test is conducted

NOTE It includes a description of test sample or test piece preparation, the instrument(s) used (calibration, adjustments, settings), the test technicians selected and the surrounding environment.

3.6
local testing

test domain comprised of one location or laboratory as typically used for quality control and internal development or evaluation programmes

3.7
global testing

test domain that encompasses two or more locations or laboratories, domestic or international, typically used for producer-user testing, product acceptance and interlaboratory test programmes

3.8
test sensitivity

⟨general⟩ derived quantity that indicates one component of technical merit of a test method, as given by the ratio of (1) the magnitude of the measured change in the property of interest, MP, for unit change in the related fundamental property, FP (i.e. the “signal”) to (2) the standard deviation in the MP measurements (i.e. the “noise”)

NOTE 1 Strictly speaking, this is the definition of absolute sensitivity (see 6.2). The change in the FP may be the difference between two actual measurements or the difference between two selected fundamental-property values. The relation between the measured property, MP, and the fundamental property, FP, is of the form $MP = f \times FP$.

NOTE 2 Although a simplified conceptual definition of test sensitivity was given in the Introduction, this more detailed but still general definition using quantitative terms is helpful for preliminary discussion purposes.

4 Measurement process

4.1 A measurement process involves three components:

- a) the chemical or physical property to be determined;
- b) a (chemical or physical) measurement system;
- c) a procedure or technique for producing the measured value.

The fundamental property to be determined, FP, has two associated adjuncts:

- the measured quantity or parameter, MP, that can take on a range of numerical values;
- the relationship between FP and MP of the general form $MP = f \times FP$.

An implicit assumption is that the procedure or technique is applicable across a range of material or system property values.

4.2 The fundamental property shall be a defined characteristic, such as the percentage of some constituent in a material or a characteristic defined solely by the measurement process itself. In the latter case, the measured property and the fundamental property are identical, i.e. $MP = FP$ or $f = 1$.

This is the usual case for many measurement operations or tests, e.g. determination of the modulus of a rubber. The relationship $MP = f \times FP$ shall be monotonic, i.e. for every value of MP there shall be a unique value of FP. The relationship shall be specific to any particular measurement process or test and, if there are two different processes or tests for determining the fundamental property, the relationship is generally different for each process or test.

5 Development of test sensitivity concepts

5.1 Test domain

The scope of any potential test sensitivity determination programme shall be established.

If local testing is the issue, the test measurements shall be conducted in one laboratory or at one location.

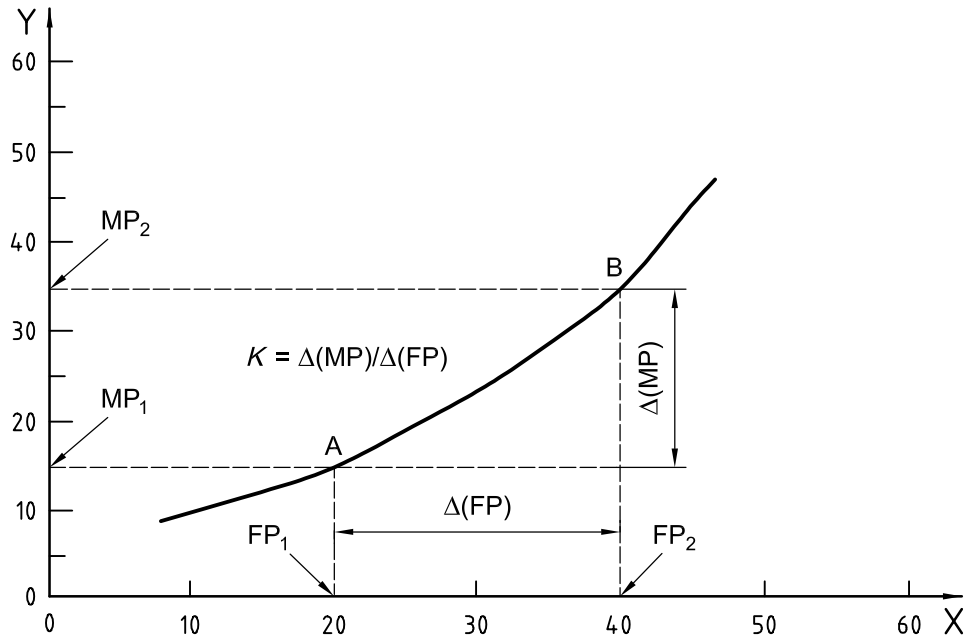
For global testing, an interlaboratory test programme (ITP) shall be conducted. Two or more replicate test sensitivity determinations shall be conducted in each participating laboratory, and an overall or average test sensitivity obtained across all the laboratories. In the context of an ITP for global testing, each replicate test sensitivity determination is defined as the entire set of operations that is required to calculate one estimated value of the test sensitivity.

For additional background on the assessment of the precision of the test sensitivity values obtained, see Annex A and ISO/TR 9272.

NOTE See also ASTM D 6600.

5.2 Absolute (class 1) test sensitivity

5.2.1 Class 1 is absolute test sensitivity, or ATS, where the word absolute is used in the sense that the measured property can be related to the fundamental property by a relationship that gives absolute or direct values of the fundamental property, FP, from a knowledge of the measured property, MP. In determining test sensitivity in this class, two or more calibration materials (CMs) are used, each having a different documented value of the FP.



Key

- X fundamental property, FP
- Y measured property, MP

Figure 1 — Relationship between measured property and fundamental property

5.2.2 Absolute test sensitivity, see Figure 1, is concerned with two types of property:

- the fundamental property (or criterion or constituent), FP, the value of which is established by the use of a calibration material, CM;
- the measured property, MP, obtained by carrying out the test method on the calibration (or another) material.

A relationship exists between the measured property and the fundamental property that can be non-linear. In carrying out a particular test, FP_1 corresponds to MP_1 and FP_2 corresponds to MP_2 . Over a selected region of the relationship, designated by points A and B in Figure 1, the slope, K , of the curve illustrated is approximately given by the relationship $K = \Delta(MP)/\Delta(FP)$. If the standard deviation for MP, denoted by σ_{MP} , is constant over this A to B range, the absolute test sensitivity, designated as ψ_A , is defined as:

$$\psi_A = \frac{|K|}{\sigma_{MP}} \tag{1}$$

The equation indicates that, in the selected region of interest, test sensitivity will increase with an increase in the numerical (absolute) value of the slope, $|K|$, and sensitivity will also increase the more precise the property measurement is. Thus ψ_A can be used as a criterion of technical merit to select one of a number of test methods to measure the fundamental property, FP, provided that a relationship $MP = f \times FP$ can be established for each test method.

5.2.3 Absolute test sensitivity may not be uniform or constant across a broad range of MP or FP values. It is constant across a specified range only if the direct (not transformed) MP vs FP relationship is linear and the test error σ_{MP} is constant. Assuming a monotonic relationship between FP and MP, the absolute test sensitivity, ψ_A , can be determined by means of:

- a) two or more calibration materials (or objects) with different known fundamental property values or
- b) a theoretical relationship between MP and FP.

5.2.4 In the completely general case, a more formal mathematical development of absolute test sensitivity that does not involve the approximation of the slope using $\Delta(\text{MP})$ and $\Delta(\text{FP})$ can be given in terms of differentials. When differentials are used, $K = |d(\text{MP})/d(\text{FP})|$ and K is the slope of the tangent to the curve at a particular point.

Annex C outlines the derivation of the absolute test sensitivity for a simple analytical test method on this more theoretical and formal basis.

5.2.5 Determining the absolute test sensitivity requires that a well-established relationship exists between MP and FP. This can be obtained in either of two ways.

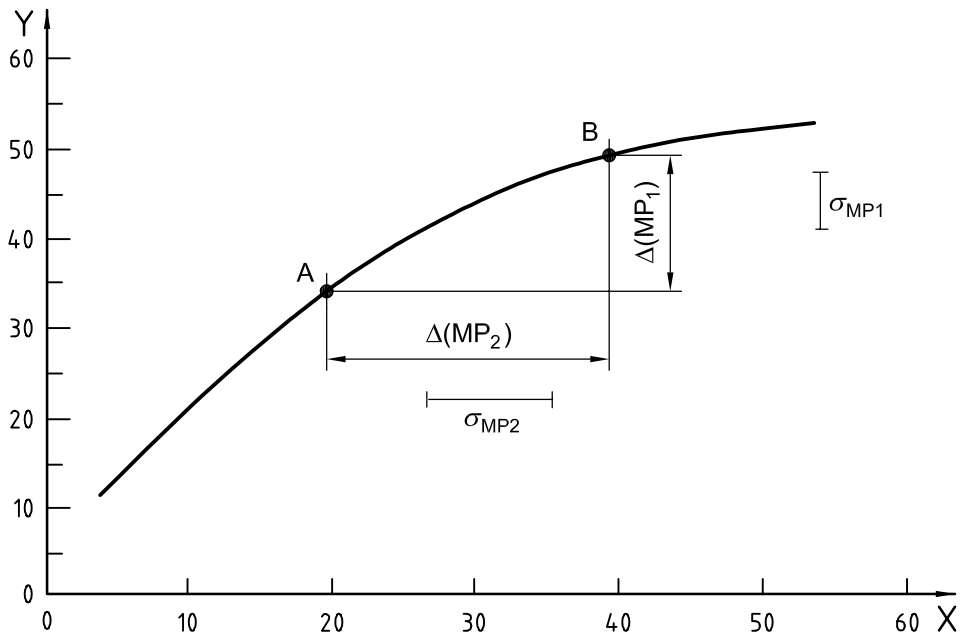
- a) An empirical determination which makes use of calibration materials, each with a different value of the FP (designated the FP calibration value), these values being certified by a recognized independent procedure or authority. The relationship between MP and FP is determined experimentally, i.e. empirically.
- b) A theoretical evaluation, conducted using the known relationship between MP and FP, and based on scientific or theoretical principles, for a measurement system that permits the calculation of FP calibration values under certain specified conditions. This will not be addressed by this International Standard since this International Standard is limited to experimental, i.e. empirical, techniques.

5.3 Relative (class 2) test sensitivity

5.3.1 A relative (i.e. class 2) test sensitivity is a sensitivity where one method is compared to another method, on the basis of a ratio, using two or more reference materials with different measured property (MP) values. This class is used for physical test methods in which no fundamental property can be determined.

When typical physical test methods are employed, establishing a relationship between MP and FP using calibration materials is not usually feasible or possible. The primary purpose of most, if not all, physical test methods is to make simple relative comparisons on the basis of the measured property values. Under these circumstances, it is not possible to determine the absolute test sensitivity.

5.3.2 If the absolute test sensitivity cannot be determined, it is possible to determine the relative sensitivities of two or more test methods. This can be accomplished without knowledge of the $\text{MP} = f \times \text{FP}$ relationship for each test method. The most simple and direct way to demonstrate how this is possible is to assume that we have two test methods for which absolute test sensitivities are known. Figure 2 illustrates the general relationship between two test methods, method 1 and method 2, with measured properties designated MP_1 and MP_2 .



Key

- X measured property MP₂
- Y measured property MP₁

Figure 2 — Relationship between two measured properties

The values of K_1 , σ_{MP1} , K_2 and σ_{MP2} are given in the following equations for ψ_{A1} and ψ_{A2} :

$$\psi_{A1} = \frac{|K_1|}{\sigma_{MP1}} \tag{2}$$

and

$$\psi_{A2} = \frac{|K_2|}{\sigma_{MP2}} \tag{3}$$

To compare the two test methods, the ratio of ψ_{A1} to ψ_{A2} is formed from Equations (2) and (3), viz:

$$\frac{\psi_{A1}}{\psi_{A2}} = \frac{\frac{|K_1|}{\sigma_{MP1}}}{\frac{|K_2|}{\sigma_{MP2}}} = \frac{|K_0| \times \sigma_{MP2}}{\sigma_{MP1}} \tag{4}$$

in which the absolute value (without regard to sign) of $K_0 (= K_1/K_2)$ is used since positive values of the ratio are desired.

5.3.3 Figure 2 illustrates the relationship between MP₁ and MP₂, with the slope given approximately by $\Delta(MP_1)/\Delta(MP_2)$ and the values of σ_{MP1} and σ_{MP2} indicated by vertical and horizontal bars, respectively. K_0 is given by

$$K_0 = \frac{|K_1|}{|K_2|} = \frac{\frac{\Delta(MP_1)}{\Delta(FP)}}{\frac{\Delta(MP_2)}{\Delta(FP)}} = \frac{\Delta(MP_1)}{\Delta(MP_2)} \tag{5}$$

since the fundamental property values, FP, although unknown, are common to both MP_1 and MP_2 and the absolute value of $\Delta(MP_1)/\Delta(MP_2)$ (without regard to sign) is used.

Thus K_0 is determined without any knowledge of the fundamental properties. The requirements are:

- that the relationship between MP_1 and MP_2 be known empirically;
- that the measurements of MP_1 and MP_2 be made on the same set of reference materials, each of which has a different FP value that is or is not known.

The relative test sensitivity for method 1 compared to method 2, designated $\psi_{R(T1/T2)}$, is expressed, as shown in Equation (6), as the ratio of test sensitivity of method 1 to that of method 2:

$$\psi_{R(T1/T2)} = \frac{\frac{\Delta(MP_1)}{\Delta(MP_2)}}{\frac{\sigma_{MP1}}{\sigma_{MP2}}} = \frac{|K_0| \times \sigma_{MP2}}{\sigma_{MP1}} \quad (6)$$

Unless needed to avoid confusion, the parenthetical term (T_1/T_2) , which represents an excessive notational burden, will be dropped and it shall be understood that the symbol ψ_R indicates a comparison between method 1 (numerator) and method 2 (denominator).

5.3.4 If ψ_R is greater than 1, method 1 is more sensitive than method 2. If ψ_R is less than 1, method 2 is more sensitive than method 1.

The relative test sensitivity is applicable to a particular intermediate range of MP_1 and MP_2 values unless the plot of MP_1 vs MP_2 is linear and the ratio $(\sigma_{MP1}/\sigma_{MP2})$ is constant across the experimental range under study. The relative test sensitivity can be expressed in more formal mathematical terms by the use of differentials rather than the delta terms $\Delta(MP_1)$ and $\Delta(MP_2)$ (see also Annex C).

5.4 Test sensitivity categories and types

5.4.1 For each of the two classes of test sensitivity, there are two sensitivity categories (category 1 and category 2) and for category 2 there are two types of test sensitivity.

5.4.2 Category 1 is a limited-range or “spot check” test sensitivity.

This is an assessment of absolute test sensitivity by a procedure that uses two (or perhaps three) different calibration materials for the fundamental-property values or for an assessment of relative test sensitivity by the use of two (or three) different reference materials. It is, in essence, a spot check in a selected measured-property range.

5.4.3 Category 2 is an extended-range test sensitivity representing a more comprehensive assessment over a substantial part or all of the entire working range of the MP vs FP values or MP_1 vs MP_2 values, as customarily used in routine testing.

Determining a category 2 absolute test sensitivity requires several calibration materials: the recommended number is 4 to 6, with several measurements of MP for each established calibration material value of the fundamental property, FP.

Determining a category 2 relative test sensitivity also requires several reference materials: the recommended number is 4 to 6, with several measurements of MP for each reference material.

5.4.4 A category 2 test sensitivity will not necessarily be uniform or constant across a broad range of values of the property measured. Thus there are two types of category 2 sensitivity:

- a) A type 1 sensitivity is one that is uniform or constant across the entire experimental range investigated. This requires a constant value for the $\sigma_{MP_1}/\sigma_{MP_2}$ ratio across this range.
- b) A type 2 sensitivity is one that is non-uniform: it depends on the value of either measured property (MP_1 or MP_2) across the experimental range. The ratio $\sigma_{MP_1}/\sigma_{MP_2}$ can usually be expressed as a linear function of either measured property (used as the x -variable) in the MP_1 vs MP_2 relationship.

6 Steps in conducting a test sensitivity determination programme

6.1 Initial decisions

6.1.1 General

The first step in any test sensitivity programme requires decisions on a number of preliminary issues. These decisions, indicated in 6.1.2 to 6.1.5, are required prior to any actual test measurement. The subsequent required steps are dependent on what decisions were made in 6.1.2 to 6.1.5, and these steps are given, on the basis of a local testing programme, in the following four subclauses of this International Standard:

- For absolute test sensitivity, Subclause 6.2 gives the steps necessary for a spot check and Subclause 6.3 gives the steps necessary for an extended-range programme.
- For relative test sensitivity, 6.4 is for a spot check and 6.5 for an extended-range programme.

NOTE Although there is some repetition in the instructions for the execution of the programme in these four subclauses, this arrangement allows the user of the standard to go directly to the subclause relevant to the requirements for the test sensitivity to be determined. Recommendations for a global evaluation programme can be found in Clause A.2 of Annex A.

6.1.2 Test method(s) to be evaluated

Select the test method(s) to be evaluated. For most programmes, there will be two or more methods since, even for absolute test sensitivity, it is likely that a comparison of the methods will be a goal of the programme. Ensure that the procedure for each test method is well defined and well documented.

6.1.3 Test domain

Define the scope of the test sensitivity programme: local for testing in one laboratory or test location or global for numerous domestic or worldwide laboratories or locations.

6.1.4 Class of test sensitivity

Select the test sensitivity class: class 1 for absolute test sensitivity and class 2 for relative test sensitivity.

6.1.5 Category of test sensitivity

Select the category of sensitivity to be determined: category 1 for a limited-range or spot check programme or category 2 for an extended-range programme.

For both category 2 absolute and category 2 relative test sensitivities, the sensitivity determined will not necessarily be uniform across the range under study. Thus it will be necessary to compile a tabulation of values of ψ_A at selected values of the fundamental property or ψ_R at selected values of the measured property.

6.2 Absolute test sensitivity in a limited-range or spot check programme

6.2.1 General

Select at least two, and preferably more, calibration materials (CMs). The difference between the measured-property (MP) values for the two (or more) CMs shall be large enough to permit the value of K (see 5.2.2) to be determined accurately. The values of the fundamental property (FP) for each CM shall be known to an accuracy sufficient for the purposes of the sensitivity determination programme. This implies that the uncertainty in the (certified) values of the FP for each CM be one-fourth or less of the uncertainty in the MP values. If the MP vs FP relationship is curvilinear or not well defined, a minimum of three CMs is required to ensure satisfactory determination of the sensitivity.

6.2.2 Number of replicate MP measurements

For each CM, conduct sufficient replicate MP measurements to establish a good estimate of the average value of the MP and the standard deviation of the measurement process. The absolute minimum number of replicates required is four, but five or six replicates are preferable. For each CM, calculate the standard deviation for the replicate MP measurements. Calculate the average, or pooled, variance across all the CMs used. The square root of this is defined as σ_{MP} .

6.2.3 Establishing the MP vs FP relationship

Determine the value of K for each test method under review (see 5.2.2).

6.2.4 Calculation of absolute test sensitivity

For each test method under consideration, calculate the absolute test sensitivity, ψ_A , from the values of $|K|$ and σ_{MP} using Equation (1) in 5.2.2. If several test methods are being evaluated, prepare a table of ψ_A values for each method for a review of the results.

6.3 Absolute test sensitivity in an extended-range programme

6.3.1 General

Select the number of calibration materials (CMs) to be used. For a good extended-range determination, a minimum of four CMs is required, but five or six are preferable. The CMs selected shall span the whole range, with approximately equal intervals between the CMs. The values of the fundamental property (FP) for each calibration material shall be known to an accuracy sufficient for the purposes of the sensitivity determination programme. This implies that the uncertainty in the (certified) values of the FP for each CM be one-fourth or less of the uncertainty in the measured-property (MP) values.

6.3.2 Number of replicate MP measurements

For each CM, conduct sufficient replicate MP measurements to establish a good estimate of the average value of the MP and the standard deviation of the measurement process. The absolute minimum number of replicates required is four, but five or six replicates are preferable. Calculate the variance and the standard deviation for each set of replicate MP measurements on each CM.

6.3.3 Standard deviations of MP measurements

Determine if there is a relationship (linear or otherwise) between the MP standard deviation for each CM and the average MP for each CM. If a statistically significant relationship exists, then ψ_A is non-uniform and varies with the value of the MP or FP across the range examined. This variation shall be taken into account in calculating ψ_A by establishing a regression equation that relates σ_{MP} to MP across the range of values used in the programme. This is of the form $\sigma_{MP} = a_0 + a_1(MP)$, where a_0 and a_1 are determined by regression analysis assuming that the relationship is approximately linear.

If there is no significant relationship between the MP standard deviation for each CM and the average MP for each CM, calculate the average, or pooled, variance for the MP across all the CMs used. The square root of this is defined as σ_{MP} .

6.3.4 Establishing the MP vs FP relationship

Generate the plot of MP vs FP and examine its nature (linear or curvilinear). The ideal outcome is a linear relationship. For curvilinear relationships, perform transformations (on one or both variables) to obtain a linear relationship. See Annex C for recommendations on applicable transformations. Once a satisfactory linear relationship has been found based on visual examination, conduct a linear regression analysis (refer to Annex A). Calculate the constant b_0 , the slope (the coefficient b), the correlation coefficient R (or R^2) and the standard deviation (or standard error of estimate), $\sigma_{y,x}$, about the fitted line. Determine the slope, K , of the MP vs FP curve, i.e. the regression coefficient, b , for each test method under review (see 5.2.2).

6.3.5 Calculation of uniform absolute test sensitivity

If σ_{MP} is invariant (constant) across the range of MP values, use the standard deviation obtained from the pooled variance for the MP measurements as the value for σ_{MP} . This calculation gives the uniform test sensitivity.

6.3.6 Calculation of non-uniform (dependent) absolute test sensitivity

If the individual MP standard deviations (across all the CMs used) are a function of either MP, the denominator in Equation (1) in 5.2.2 will vary with the value of the MP. This requires an expression of the form $a_0 + a_1(\text{MP})$ as given in 6.3.3 above, in which the numerical values obtained from analysis are substituted for a_0 and a_1 . In such a case, report ψ_A as a non-uniform (dependent) absolute test sensitivity and prepare a table giving the value of ψ_A for each of several selected values of the MP across the entire experimental range. If several test methods are being evaluated, prepare, for each method, a table of ψ_A values at some reference value of the MP, such as the middle of the MP range. This permits the test sensitivities of all the methods under consideration to be compared on a common basis.

6.4 Relative test sensitivity in a limited-range or spot check programme

6.4.1 General

Select the two (or more) reference materials (RMs) to be used. It is not required that a certified fundamental property (FP) value be known for each RM. It is sufficient to know an approximate value of the FP for each RM. The difference between the measured property (MP) values for the two (or more) RMs shall be large enough to permit reliable determination of the slope, K_0 , as given by Equation (5) in 5.3.3. If the MP vs FP relationship is curvilinear or not well defined, a minimum of three CMs is required to determine the sensitivity accurately.

6.4.2 Number of replicate MP measurements

For each RM, conduct sufficient replicate MP measurements for each of the test methods under review to establish a good estimate of the average value of the standard deviation of the measurement process. The absolute minimum number of replicates required is four, but five or six replicates are preferable, especially for a limited-range evaluation. For each test method, calculate the standard deviation of each set of replicate MP measurements and the average, or pooled, variance across all the RMs used. The square root of the pooled variance for test method 1, T_1 , is defined as σ_{MP1} and the square root of the pooled variance for test method 2, T_2 , is defined as σ_{MP2} .

6.4.3 Establishing the MP_1 vs MP_2 relationship

Determine the slope, K_0 , for each test method under review using $\Delta(\text{MP})$ values as given by Equation (5) in 5.3.3. This assumes that only two RMs are being used. If three RMs are being used, determine the slope by linear regression analysis assuming that the MP_1 vs MP_2 relationship is approximately linear.

6.4.4 Calculation of relative test sensitivity

For each test method under consideration, calculate ψ_R from the values of $|K_0|$ and the ratio $\sigma_{MP1}/\sigma_{MP2}$ using Equation (6) in 5.3.3. If several test methods are being evaluated, select one of the methods as a reference or standard method and use this as T_2 (the denominator in the T_1/T_2 ratio) for all relative test sensitivity calculations. Thus with three test methods, there will be three ψ_R values: $\psi_{R(T1/T2)}$ for method 1 compared to method 2, $\psi_{R(T3/T2)}$ for method 3 compared to method 2 and $\psi_{R(T2/T2)}$ which by definition is 1,00. Compare the numerical values of $\psi_{R(T1/T2)}$ and $\psi_{R(T3/T2)}$ with 1,00 to determine which of the three methods has the highest test sensitivity.

6.5 Relative test sensitivity in an extended-range programme

6.5.1 General

Select the number of reference materials (RMs) to be used. For a good extended-range determination, a minimum of four RMs is required, but five or six are preferable. The RMs selected shall span the whole range, with approximately equal intervals between the RMs. Approximate values of the measured property (MP) or fundamental property (FP) will therefore have to be known for each RM.

6.5.2 Number of replicate MP measurements

For each test method, conduct sufficient replicate measurements on each RM to establish a good estimate of the standard deviation of the measurement process for each of the MPs (MP_1 , MP_2 , etc.). The absolute minimum number of replicates required is four, but five or six replicates are preferable. If more than two test methods are being evaluated, select one method as the reference or standard method and use it as a reference to compare ψ_R for all the methods. For each method, calculate the variance and standard deviation for each set of replicate MP measurements on each RM.

6.5.3 MP measurement standard deviations

For each test method, determine if there is a relationship (linear or otherwise) between the standard deviation (for each RM) and either or both MPs. This is for general background information. Next calculate the ratio $\sigma_{MP1}/\sigma_{MP2}$ for each RM and determine if this ratio is a function of either MP. If a statistically significant relationship exists, then ψ_R is non-uniform and varies with the value of the MP across the range examined. Establish a regression equation of the form $\sigma_{MP1}/\sigma_{MP2} = a_0 + a_1(MP)$, where a_0 and a_1 are determined by regression analysis assuming that the relationship is approximately linear.

6.5.4 Establishing the MP_1 vs MP_2 relationship

The next operation is to establish a relationship between the two MPs. For this relationship or plot, take as the x -variable the MP with the smaller pooled variance for the MP measurements across all the RMs. Plot this MP against the other MP (as the y -variable) and examine the nature of the plot (linear or curvilinear). The ideal outcome is a linear relationship. For curvilinear relationships, perform transformations (on one or both variables) to obtain a linear relationship. See Annex C for recommendations on applicable transformations.

6.5.5 Estimating K_0

Once a satisfactory linear relationship (original or transformed) has been found based on visual examination, calculate the constant b_0 , the slope (the coefficient b), the correlation coefficient R (or R^2) and the standard deviation (or standard error of estimate), $\sigma_{y,x}$, about the fitted line (see Annex A). The slope, K_0 , given by Equation (5) in 5.3.3, is equal to the regression coefficient, b , for each test method under review.

6.5.6 Calculation of uniform relative test sensitivity

If $\sigma_{MP1}/\sigma_{MP2}$ is invariant (constant) across the range of MP values, use the overall average $\sigma_{MP1}/\sigma_{MP2}$ obtained from the pooled variances to calculate the uniform relative test sensitivity ψ_R .

6.5.7 Calculate the non-uniform (dependent) relative test sensitivity

If the ratio $\sigma_{MP1}/\sigma_{MP2}$ varies with the value of either measured property, an expression of the form $\sigma_{MP1}/\sigma_{MP2} = a_0 + a_1(MP)$, as given in 6.3.3, is required for the denominator of Equation (6) in 5.3.3. This assumes that a linear expression is a good approximation. The values used for a_0 and a_1 are those obtained from the analysis and the value of MP shall be a transformed value. In such a case, report ψ_R as a non-uniform (dependent) test sensitivity and prepare a table giving the value of ψ_R for each of several selected values of the MP across the entire experimental range. If several test methods are being evaluated, prepare, for each method, a table of ψ_R values at some reference value of the MP, such as the middle of the MP range. This permits the test sensitivities of all the methods under consideration to be compared on a common basis.

7 Test sensitivity report

A report of the results of the test sensitivity determination shall be prepared. This is required due to the various classes, categories and types of test sensitivity that are under investigation.

The report shall include the following:

- a) a reference to this International Standard;
- b) the test method(s) under investigation;
- c) the CMs or RMs used for the programme and their certified FP values or approximate RM values;
- d) the class of test sensitivity determined: absolute or relative;
- e) the category of test sensitivity determined: limited-range (spot check) or extended-range (in which case give the range);
- f) the type of test sensitivity obtained: uniform or non-uniform (dependent);
- g) any transformations made;
- h) a tabulation of the one or more uniform or non-uniform (dependent) test sensitivities;
- i) the standard deviations of the test sensitivities, if determined;
- j) the date(s) of the investigation.

Annex A (informative)

Background information on linear regression analysis and precision of test sensitivity determinations

A.1 Linear regression analysis

A.1.1 Once an apparent linear relationship between MP_1 and FP or MP_1 and MP_2 has been found (if necessary, using transformations), a decision on the goodness of fit for the particular relationship selected can be made. The recommended procedure is not exact, but a first-order approximation that is suitable for most circumstances. Form a ratio of:

- a) the pooled measurement variance (across all calibration materials or reference materials) for the MP chosen as the x -variable, and
- b) the variance of the regression estimate (standard error of estimate squared).

If the ratio of these two variances is of the order of 4 or less, the fit can be considered as acceptable and the particular relationship adopted as a reasonable approximation for determining the slope K or K_0 . If the ratio is above 4, another, better-fitting, relationship should be found.

A.1.2 One of the assumptions in classic linear regression analysis is that each x -value is known with zero or a very small error compared to the variation in the y -variable. The typical relative test sensitivity determination does not conform to this requirement, however, since both measured properties are subject to test error. The recommended procedure to address this is to select, for the x -variable, the measured property that has the lowest pooled variance across all the calibration materials or reference materials used in the programme. This produces a minimum error estimate for the linear regression b -coefficient or slope of the MP vs FP or MP_1 vs MP_2 relationship.

A.1.3 Most relative test sensitivity programmes are conducted with one of the measured properties pre-selected as the basis or standard for comparison, i.e. T_2 in the parameter $\psi_{R(T_1/T_2)}$, which is of course the measured property that corresponds to the x -value. If T_2 has a higher pooled variance than T_1 , the procedure to follow is to conduct the regression analysis on the basis $x = T_1 = MP_1$ and $y = T_2 = MP_2$ and obtain the slope or regression coefficient designated as b_{T_2/T_1} . This coefficient is the inverse of the coefficient b_{T_1/T_2} and, after the analysis has been conducted, the reciprocal of b_{T_2/T_1} is obtained and used as the best estimate of b_{T_1/T_2} . This operation reduces the perturbing influence of the x -variation on the b -coefficient estimate. If the variance ratio T_{\max}/T_{\min} is not substantially different from unity (of the order of 4 or less), the difference in the b -coefficient estimates is not great.

A.2 Precision of test sensitivity determination

A.2.1 Test sensitivity is determined on the basis of experimentally measured parameters, and the precision of any test sensitivity estimate depends on the precision of these measurements.

For ψ_A , there are two parameters: the slope, K , of the MP_1 vs FP relationship and the standard deviation σ_{MP} . For ψ_R , there are three parameters: the slope, K_0 , of the MP_1 vs MP_2 relationship and the standard deviations σ_{MP1} and σ_{MP2} .

It is possible to relate the uncertainty in ψ_A and ψ_R to the uncertainties in the measured parameters by means of propagation of random error equations.

However, this is not addressed in this International Standard for two reasons:

- a) it adds a measure of complexity that is beyond the scope of the standard;
- b) it does not necessarily yield a true estimate of the real uncertainty in determining ψ_A and ψ_R .

A.2.2 The system of causes and effects that generates uncertainty in either ψ_A or ψ_R includes variation in individual set-up operations in addition to the actual test measurement variation *per se*.

The uncertainty in any ψ_A and ψ_R value depends on:

- a) the actual calibration materials or reference materials used;
- b) the status of these materials (whether they are RMs or CMs);
- c) the operators used for the testing;
- d) the ambient laboratory operating conditions (which will affect the accuracy of instrument calibrations).

For a reliable estimate of the uncertainty in ψ_A and ψ_R , such components of variation should be included in the precision programme to make it realistic.

A.3 Determination of test sensitivity, uncertainty or confidence levels

A.3.1 General

The recommended procedure for determining test sensitivity, uncertainty or confidence levels is as follows:

A.3.2 Local determination of test sensitivity

For a local absolute or relative test sensitivity, repeat the total determination of either ψ_A or ψ_R a sufficient number of times to obtain a good estimate of the standard deviation for either test sensitivity. If ψ_A or ψ_R can be fully evaluated in one day, conduct four separate complete determinations (of the total operation) over a period of several days. This is a bare-minimum estimate of the test sensitivity standard deviation. It is much preferable, however, to obtain six or more estimates of ψ_A or ψ_R .

Use these standard deviation estimates to calculate confidence intervals or to conduct statistical-significance tests (*t*-tests) for the difference $\psi_A - 1,00$ or $\psi_R - 1,00$, since a value of unity for ψ_A or ψ_R implies that there is no difference in the test sensitivity of one method, T_1 , compared to another, T_2 . More sophisticated multiple comparisons, such as Duncan's multiple range test, can be employed to compare more than two ψ_A or ψ_R estimates.

A.3.3 Global determination of test sensitivity

For a global determination of test sensitivity, the procedures and protocols as developed for interlaboratory precision should be followed (see ISO/TR 9272). One or more experienced staff members in one laboratory should be selected to organize the global programme. Select a number of laboratories that have good experience with the test methods. Set aside a sufficient quantity of a homogeneous lot of each reference material and send samples to each participating laboratory. Two individual or separate test sensitivity determinations (all required steps completed) should be conducted in each laboratory on the basis of this International Standard, using the reference materials supplied. The two separate evaluations should be one week apart. The resulting database can be analysed using the procedures outlined in ISO/TR 9272. The outcome from such testing will give a global average for ψ_A or ψ_R and a between-laboratory uncertainty or confidence limit for the average values.

Annex B (informative)

Two examples of relative test sensitivity determinations

B.1 Example 1: Processability test methods — Determination of limited-range (spot check) relative sensitivities

B.1.1 In this example, a limited-range, or “spot check”, relative test sensitivity is determined for three different processability test methods. The use of more than two methods illustrates the general procedure for multiple comparisons of sensitivities. The data and calculations are given in Table B.1 and Table B.2. The three processability methods used to generate processability numbers are designated P_1 , P_2 and P_3 and two reference materials (RM_1 and RM_2) are used with four replications of the “processability number” (Proc number), R_1 to R_4 , for each RM and each method. In Table B.1, the average, the variance and the standard deviation (Avg, Var, S dev) for the processability numbers are listed for each reference material and each method. For each method, the pooled (average) variance and the standard deviation obtained from the pooled variance, as well as the coefficient of variation, in percent, are also listed.

B.1.2 Table B.2 lists the calculated parameters and the relative test sensitivity or ψ_R values. For each test method, the value of Δ is given, where $\Delta = (\text{Avg proc number for } RM_2 - \text{Avg proc number for } RM_1)$. This corresponds to the ΔMP values discussed in the main text of the standard. Also listed are the pooled standard deviation, the ratio Δ_1/Δ_2 which is equal to $K_{0(1,2)}$ (where subscripts 1 and 2 refer to P_1 and P_2) and the ratio Δ_3/Δ_2 which is equal to $K_{0(3,2)}$ (where subscripts 3 and 2 refer to P_3 and P_2). The ratios σ_1/σ_2 and σ_2/σ_3 are also given, where σ_1 , σ_2 and σ_3 refer to the (pooled) standard deviations for P_1 , P_2 and P_3 .

B.1.3 Using these values, calculations of relative test sensitivity give $\psi_{R(P_1/P_2)}$ for P_1 relative to P_2 and $\psi_{R(P_3/P_2)}$ for P_3 relative to P_2 . It is found that $\psi_{R(P_1/P_2)} = 0,96$ and $\psi_{R(P_3/P_2)} = 1,26$. To review all three processability test methods on the same comparative scale, the value 1 is assigned to the test sensitivity of the reference (or denominator) method, P_2 , since $\psi_{R(P_2/P_2)} = 1,00$. The last column in Table B.2 gives the comparative value, Comp ψ_R , for P_1 and P_3 versus P_2 . The relative sensitivities, $\psi_{R(P_1/P_2)}$ and $\psi_{R(P_2/P_2)}$ for test P_1 and P_2 , are very similar at 0,96 and 1,00, respectively, with only a 4 % difference between them, while P_3 is the most sensitive method; with $\psi_{R(P_3/P_2)} = 1,26$. Method P_3 is thus 26 % more sensitive than P_2 .

B.1.4 The coefficient of variation values for P_1 , P_2 and P_3 (i.e. 2,06, 1,37, 1,30) can be used to determine an index of technical merit for the three processability tests based on precision alone. For this, technical merit is assumed to be proportional to the reciprocal of the coefficient of variation, i.e. the higher the coefficient the less the technical merit. The reciprocal values are 0,49, 0,73 and 0,77 for P_1 , P_2 and P_3 , respectively. When these three reciprocal coefficient of variation values are put on the same comparison basis as the comp ψ_R values, this gives 0,67, 1,00, 1,05 for P_1/P_2 , P_2/P_2 and P_3/P_2 . Although these precision technical merit indexes indicate P_3 to be the best and P_1 to be the worst processability test (assuming numerical differences to be statistically significant) which is the same qualitative ranking as the Comp ψ_R sensitivity values of 0,96, 1,00 and 1,26, the magnitude of the differences compared to the reference P_2 test are substantially different for tests P_1 and P_3 . This demonstrates the inability of coefficient of variation (and standard deviation and variance as well) to give a useful quantitative indication of test sensitivity for this particular test.

B.1.5 As discussed in the text of the standard, these ψ_R values are estimated values that are subject to sampling and inherent test error variation. The difference in ψ_R of 0,04 between P_1 and P_2 is probably within expected test error, and the difference between the sensitivities of these two processability test methods is probably not statistically significant. The difference of 0,26 between P_3 and P_2 , on the other hand, is probably statistically significant. For definitive statements on the statistical significance of ψ_R values, sufficient repeat determinations of the entire ψ_R determination process on several days are required to generate a number of estimates (four or more) to be able to make decisions based on the usual statistical procedures for differences in mean values.

Table B.1 — Determination of limited-range relative sensitivity of three processability test methods — Basic “processability number” data for RM₁ and RM₂ for methods P₁, P₂ and P₃

RM	Processability test method 1						
	R ₁	R ₂	R ₃	R ₄	Avg	Var	S dev
RM ₁	4,50	4,65	4,60	4,70	4,61	0,005 47	0,074
RM ₂	3,10	3,00	2,90	3,10	3,03	0,006 87	0,083
				Δ	- 1,59		
				Avg	3,82		
Pooled values						0,006 17	0,079
Coeff. var, % (σ ₁ = 0,079)					2,06		
RM	Processability test method 2						
	R ₁	R ₂	R ₃	R ₄	Avg	Var	S dev
RM ₁	9,10	8,90	9,30	9,00	9,08	0,021 88	0,148
RM ₂	12,10	12,30	11,90	12,10	12,10	0,020 00	0,141
				Δ	3,03		
				Avg	10,59		
Pooled values						0,020 94	0,145
Coeff. var, % (σ ₂ = 0,145)					1,37		
RM	Processability test method 3						
	R ₁	R ₂	R ₃	R ₄	Avg	Var	S dev
RM ₁	10,10	10,30	9,90	9,80	10,03	0,036 88	0,192
RM ₂	14,20	14,10	14,30	14,00	14,15	0,012 50	0,112
				Δ	4,13		
				Avg	12,09		
Pooled values						0,024 69	0,157
Coeff. var, % (σ ₃ = 0,157)					1,30		
NOTE	Δ = Avg No. for RM ₂ – Avg No. for RM ₁ ;						
	σ ₁ = S dev for P ₁ , σ ₂ = S dev for P ₂ and σ ₃ = S dev for P ₃ .						

Table B.2 — Determination of limited-range relative sensitivity of three processability test methods — Calculated parameters and ψ_R values for P_1 , P_2 and P_3

Test method	Δ	Pooled S dev	$K_{0(1,2)}$	$K_{0(3,2)}$	σ_1/σ_2	σ_3/σ_2	Comp ψ_R
P_1	- 1,59	0,079	- 0,525		0,545		0,96
P_2	3,03	0,145					1,00
P_3	4,14	0,157		1,363		1,083	1,26

$K_{0(1,2)} = \Delta_1/\Delta_2$
 $K_{0(3,2)} = \Delta_3/\Delta_2$
 Comp ψ_R = value of ψ_R for P_1 and P_3 assuming a value of ψ_R of 1,00 for P_2 .
 Calculation of ψ_R values:
 $\psi_{R(P1/P2)} = K_{0(1,2)}/(\sigma_1/\sigma_2) = |(- 1,59/3,03)|/(0,079/0,145) = 0,96$
 $\psi_{R(P3/P2)} = K_{0(3,2)}/(\sigma_3/\sigma_2) = |(4,14/3,03)|/(0,157/0,145) = 1,26$

B.2 Example 2: Test methods for compliance and modulus — Determination of extended-range relative sensitivities

B.2.1 In this example, the relative test sensitivity is determined of methods of measuring two different physical properties for evaluating characteristics such as the degree of cure of rubbers. Test method 1 is a compliance determination, i.e. measurement of the deformation or strain of a test piece under a fixed or constant force, and test method 2 is a modulus determination, i.e. measurement of the stress under a fixed (constant) extension or strain. The magnitude of ψ_R is determined over a range of values for each test method: high compliance corresponds to low modulus and *vice versa*. Tables B.3 to B.5 give the data generated by the sensitivity determination programme. Six reference materials, designated A to F, with a range of compliance and modulus values, were tested, using deformations and stresses characteristic of the two methods. For each method and each reference material, four replicate measurements, R_1 to R_4 , were made. Table B.3 gives the values of these measurements, as well as the average and standard deviation for each reference material for both properties.

B.2.2 The plot in Figure B.1 shows the curvilinear inverse relationship between compliance and modulus. All four replicate values obtained with each reference material are shown on the plot. Since a linear relationship is required to simplify the determination of ψ_R , transformation of the compliance and modulus data is needed. Table B.4 gives the log-transformed average, variance, standard deviation and coefficient of variation values for both measured properties. Figure B.2 shows that a reasonably good linear relationship is obtained for the plot of log compliance vs log compliance. Transformation of the original compliance and modulus data can be carried out without concern for any possible effect on the relative sensitivity since, as shown in Annex C, such a transformation does not alter the relative sensitivity.

B.2.3 Table B.5 gives the results of a sorting operation on the transformed data in Table B.4 (low to high, by the average value of log compliance and log modulus for the reference material). This shows that the variance, standard deviation and coefficient of variation (among the four replicates for each RM) increase as the compliance increases and, conversely, the variation decreases as the modulus increases. This dependence of variation on average value for the RM is also suggested by the log transformation as discussed above in B.2.2. This behaviour will be discussed below in the context of the non-constancy of ψ_R in this measurement system across the range of reference material values.

B.2.4 Table B.6 and Table B.7 give the log data values for all four replicates for each of the six reference materials in a tabular format that is convenient for linear regression analysis. This determination (as in most other such determinations) does not obey the “zero error in x ” regression assumption since both physical properties are subject to test error. The procedure recommended in Annex A to address this is to select, as the x -variable, the measured property that has the smaller pooled variance across all the RMs used in the programme.

B.2.5 A review of the pooled variances in Table B.4 shows that the pooled variance for log compliance is 0,000 079 1 and that for log modulus is 0,000 025 3, i.e. a compliance variance to modulus variance ratio of 3,13. Thus modulus should be the x -variable. Although not strictly required, Table B.6 is presented to illustrate the dual regression calculation procedure as discussed in Annex A. It gives the results of two sets of linear regression calculations: No. 1 for log compliance vs log modulus (as y and x) and No. 2 for log modulus vs log compliance (as y and x). The regression x -coefficients (i.e. slopes) indicated by $b_{C/M}$ for calculation No. 1 and by $b_{M/C}$ for calculation No. 2 are given in Table B.6, where C = compliance and M = modulus.

B.2.6 The value of $b_{C/M}$ is $-1,844$ and that of the inverse regression, $b_{M/C}$, is $-0,540$. Since the two b -coefficients are inversely related to each other, the reciprocal of $b_{M/C}$ gives a second estimate of $b_{C/M}$, viz $1/-0,540 = -1,853$. The difference between $-1,844$ and $-1,853$ represents the influence (on the slope estimate) of the variation in x generated by the modulus values compared with the variation in x generated by the compliance values. The estimates are reasonably close since the variance ratio is not much greater than 1. The better b -coefficient estimate is $-1,84$ (rounded) and this is the one used. The slope (the coefficient b) is equal to $d(MP_1)/d(MP_2)$ (or $\Delta MP_1/\Delta MP_2$) as discussed in the text of the standard, and is thus equal to K_0 .

B.2.7 Table B.7 shows the calculation of the ratio $\sigma_{MP1}/\sigma_{MP2}$ as previously discussed in the standard. This ratio is indicated in Table B.7 as σ_1/σ_2 , where σ_1 is the standard deviation of log compliance and σ_2 is the standard deviation of log modulus. Table B.7 also gives the values of the average value and standard deviation of log compliance and log modulus, and the σ_1 to σ_2 ratio, for each reference material. Figure B.3 shows the plot of standard deviation of log compliance vs log compliance and Figure B.4 the plot of standard deviation of log modulus vs log modulus. These have opposite slopes, of course, as expected. Figures B.5 and B.6 show that the ratio σ_1/σ_2 is also a linear function of both log compliance and log modulus, again with opposite slopes. The right-hand side of Table B.7 gives the output of the linear regression analysis of σ_1/σ_2 vs log modulus. The slope or x -coefficient of this relationship is $-1,89$ and the constant is $2,76$.

B.2.8 The relative test sensitivity, $\psi_{R(T1/T2)}$, where T_1 indicates compliance and T_2 indicates modulus, or $\psi_{R(C/M)}$, is equal to $|K_0|/(\sigma_1/\sigma_2)$. We have seen that the ratio σ_1/σ_2 changes with the level of either compliance or modulus and thus $\psi_{R(C/M)}$ does not have a fixed or constant value. It is a function of log modulus and is given by the following equation:

$$\psi_{R(C/M)} = |K_0|/[2,76 - 1,89 \times (\log \text{ modulus})]$$

Table B.8 gives values of $\psi_{R(C/M)}$ at selected log modulus values that span the experimental range used for this programme. At the lowest log modulus value of 0,40 (high compliance), $\psi_{R(C/M)}$ is 0,92, i.e. the modulus test method is slightly more sensitive than the compliance test method. As the value of the modulus increases, $\psi_{R(C/M)}$ increases to greater than 1, and the compliance method becomes more sensitive than the modulus method. At the highest log modulus value of 0,80, the compliance method is 47 % more sensitive than the modulus method.

B.2.9 As with Example 1 for the "spot check" relative test sensitivity, each extended-range $\psi_{R(C/M)}$ value in Table B.8 is an estimate obtained from one replicate of the *entire* test sensitivity determination which uses six reference materials and four measurement replicates for each reference material. To be able to assign uncertainty or confidence limits to $\psi_{R(C/M)}$ it would be necessary to repeat the entire relative test sensitivity programme a sufficient number of times to be able to calculate reliable standard deviations for $\psi_{R(C/M)}$ values at selected modulus or compliance levels.

Table B.3 — Determination of extended-range relative sensitivity of compliance and modulus test methods — Data obtained from programme

RM	Compliance						Modulus					
	R ₁	R ₂	R ₃	R ₄	Avg	S dev	R ₁	R ₂	R ₃	R ₄	Avg	S dev
A	8,30	8,25	8,15	8,30	8,25	0,070 7	5,45	5,52	5,52	5,53	5,51	0,037 0
B	28,55	27,55	29,50	28,15	28,44	0,818 9	2,74	2,82	2,72	2,77	2,76	0,043 5
C	11,25	11,02	11,35	11,25	11,22	0,139 9	4,56	4,64	4,61	4,63	4,61	0,035 6
D	14,15	13,95	13,71	13,95	13,94	0,180 0	4,12	4,18	4,20	4,17	4,17	0,034 0
E	24,65	23,60	24,83	25,10	24,55	0,656 6	3,09	3,14	3,06	3,04	3,08	0,043 5
F	20,25	19,40	19,27	20,00	19,73	0,470 4	3,49	3,55	3,59	3,49	3,53	0,049 0
Avg or pooled	17,86	17,30	17,80	17,79	17,69		3,91	3,98	3,95	3,94	3,94	

Table B.4 — Log-transformed data

RM	Log compliance							
	R ₁	R ₂	R ₃	R ₄	Avg	Var	S dev	CV, %
A	0,919	0,916	0,911	0,919	0,916	0,000 013 9	0,003 73	0,41
B	1,456	1,440	1,470	1,449	1,454	0,000 155 2	0,012 46	0,86
C	1,051	1,042	1,055	1,051	1,050	0,000 029 4	0,005 43	0,52
D	1,151	1,145	1,137	1,145	1,144	0,000 031 5	0,005 61	0,49
E	1,392	1,373	1,395	1,400	1,390	0,000 137 9	0,011 74	0,85
F	1,306	1,288	1,285	1,301	1,295	0,000 106 2	0,010 31	0,80
Avg or pooled	1,212	1,201	1,209	1,211	1,208	0,000 079 1	0,008 21	0,65
RM	Log modulus							
	R ₁	R ₂	R ₃	R ₄	Avg	Var	S dev	CV, %
A	0,736	0,742	0,742	0,743	0,741	0,000 008 6	0,002 93	0,39
B	0,438	0,450	0,435	0,442	0,441	0,000 046 5	0,006 82	1,54
C	0,659	0,667	0,664	0,666	0,664	0,000 011 3	0,003 36	0,51
D	0,615	0,621	0,623	0,620	0,620	0,000 012 6	0,003 56	0,57
E	0,490	0,497	0,486	0,483	0,489	0,000 036 8	0,006 07	1,24
F	0,543	0,550	0,555	0,543	0,548	0,000 036 2	0,006 02	1,10
Avg or pooled	0,580	0,588	0,584	0,583	0,584	0,000 025 3	0,004 79	0,89

Table B.5 —Sorted log-transformed data

RM	Log compliance sorted by avg log compliance							
	R ₁	R ₂	R ₃	R ₄	Avg	Var	S dev	CV, %
A	0,919	0,916	0,911	0,919	0,916	0,000 013 9	0,003 73	0,41
C	1,051	1,042	1,055	1,051	1,050	0,000 029 4	0,005 43	0,52
D	1,151	1,145	1,137	1,145	1,144	0,000 031 5	0,005 61	0,49
F	1,306	1,288	1,285	1,301	1,295	0,000 106 2	0,010 31	0,80
E	1,392	1,373	1,395	1,400	1,390	0,000 137 9	0,011 74	0,85
B	1,456	1,450	1,470	1,449	1,454	0,000 155 2	0,012 46	0,86
Avg or pooled	1,212	1,201	1,209	1,211	1,208	0,000 079 1	0,008 21	0,65
RM	Log modulus sorted by avg log modulus							
	R ₁	R ₂	R ₃	R ₄	Avg	Var	S dev	CV, %
B	0,438	0,450	0,435	0,442	0,441	0,000 046 5	0,006 82	1,54
E	0,490	0,497	0,486	0,483	0,489	0,000 036 8	0,006 07	1,24
F	0,543	0,550	0,555	0,543	0,548	0,000 036 2	0,006 02	1,10
D	0,615	0,621	0,623	0,620	0,620	0,000 012 6	0,003 56	0,57
C	0,659	0,667	0,664	0,666	0,664	0,000 011 3	0,003 36	0,51
A	0,736	0,742	0,742	0,743	0,741	0,000 008 6	0,002 93	0,39
Avg or pooled	0,580	0,588	0,584	0,583	0,584	0,000 025 3	0,004 79	0,89

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Table B.6 — Calculation of K_0

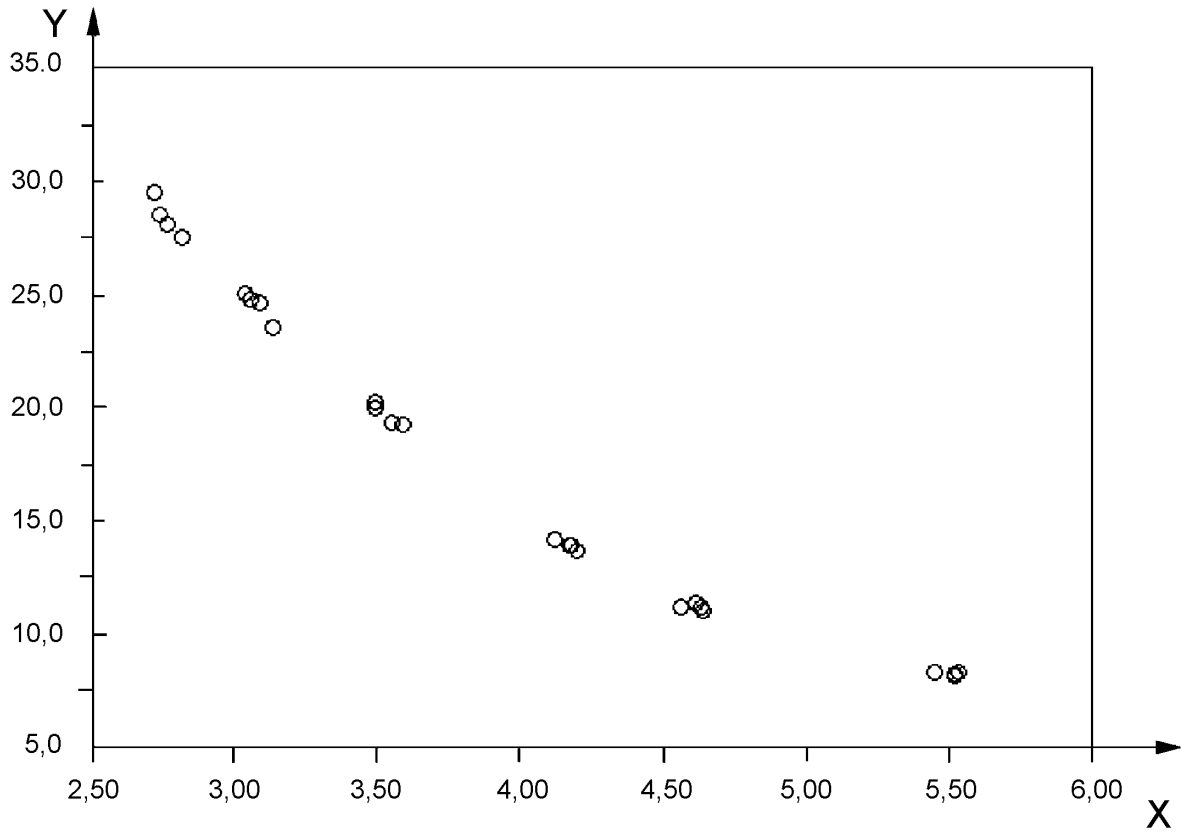
RM	Log modulus	Log compliance	Linear regression calculations	
A	0,736	0,919	Calculation No. 1: $y = \log \text{comp}; x = \log \text{mod}$	
	0,742	0,916		
	0,742	0,911		
	0,743	0,919	Regression analysis output:	
B	0,438	1,456	Constant	2,28
	0,450	1,440	Std error of y -estimate	0,013 3
	0,435	1,470	R^2	0,995
	0,442	1,449	No. of observations	24
C	0,659	1,051	Degrees of freedom	22
	0,667	1,042	x -Coefficient $b_{C/M}$	- 1,844
	0,664	1,055	Std error of coeff.	0,026
	0,666	1,051		
D	0,615	1,151	Calculation No. 2: $y = \log \text{mod}; x = \log \text{comp}$	
	0,621	1,145		
	0,623	1,137		
	0,620	1,145	Regression analysis output:	
E	0,49	1,392	Constant	1,236
	0,497	1,373	Std error of y -estimate	0,007 2
	0,486	1,395	R^2	0,995
	0,483	1,400	No. of observations	24
F	0,543	1,306	Degrees of freedom	22
	0,550	1,288	x -Coefficient $b_{M/C}$	- 0,540
	0,555	1,285	Std error of coeff.	0,007 7
	0,543	1,301		
Pooled "within RM"			Reciprocal of $b_{M/C}$ (= $1/- 0,540$)	- 1,853
Variance	0,000 025 3	0,000 079 1	Therefore $K_0 =$	1,84 (absolute)
Std deviation	0,005 03	0,008 89	(See discussion in B.2.6.)	
Variance ratio	3,13			

Table B.7 — Calculation of standard deviation ratio σ_1/σ_2

RM	Log compliance		Log modulus		Ratio σ_1/σ_2	Regression analysis output: $y = \sigma_1/\sigma_2; x = \log \text{ modulus}$	
	Avg	S dev	Avg	S dev			
A	0,916	0,003 73	0,741	0,002 93	1,28	Constant	2,76
B	1,454	0,012 46	0,441	0,006 82	1,83	Std error of y-estimate	0,098 0
C	1,050	0,005 43	0,664	0,003 36	1,61	R^2	0,854
D	1,144	0,005 61	0,620	0,003 56	1,58	No. of observations	6
E	1,390	0,011 74	0,489	0,006 07	1,94	Degrees of freedom	4
F	1,295	0,010 31	0,548	0,006 02	1,71	x-Coefficient	- 1,89
						Std error of coeff.	0,391
$\sigma_1 =$ S dev of log compliance $\sigma_2 =$ S dev of log modulus			Defining equation: $\sigma_1/\sigma_2 = 2,76 - 1,89 \times (\log \text{ modulus})$				

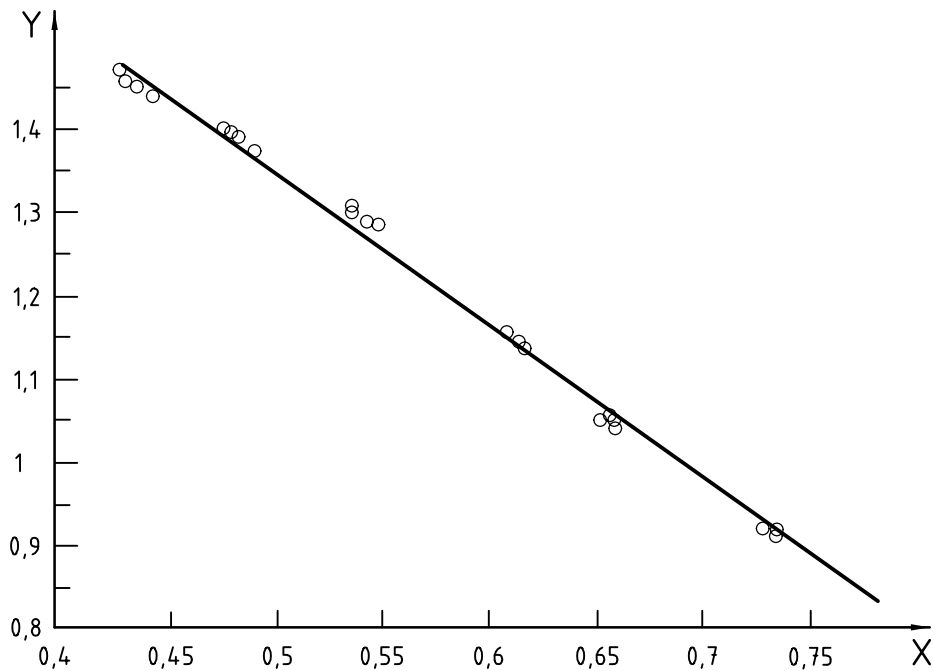
Table B.8 — Calculation of relative test sensitivity

Log modulus	$\psi_{C/M}$
0,40	0,92
0,50	1,01
0,60	1,13
0,70	1,28
0,80	1,47
Defining equation:	
$\psi_{C/M} = \frac{ K_0 \times \sigma_2}{\sigma_1} = \frac{1,84}{2,76 - 1,89 \times (\log \text{ modulus})}$	



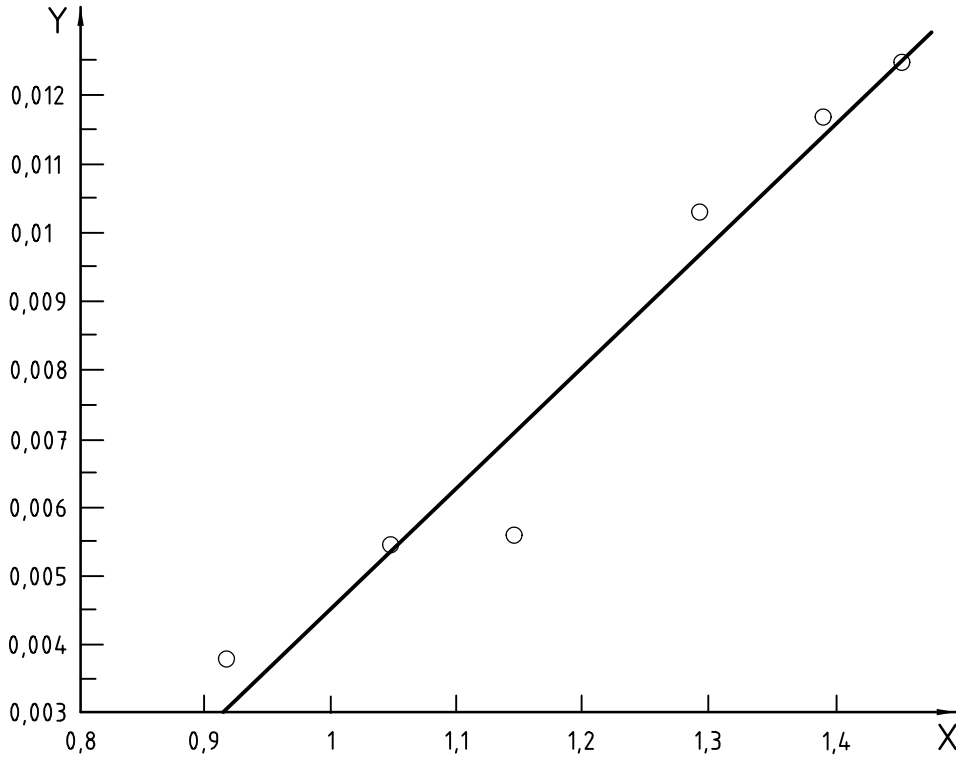
Key
 X modulus
 Y compliance

Figure B.1 — Compliance vs modulus



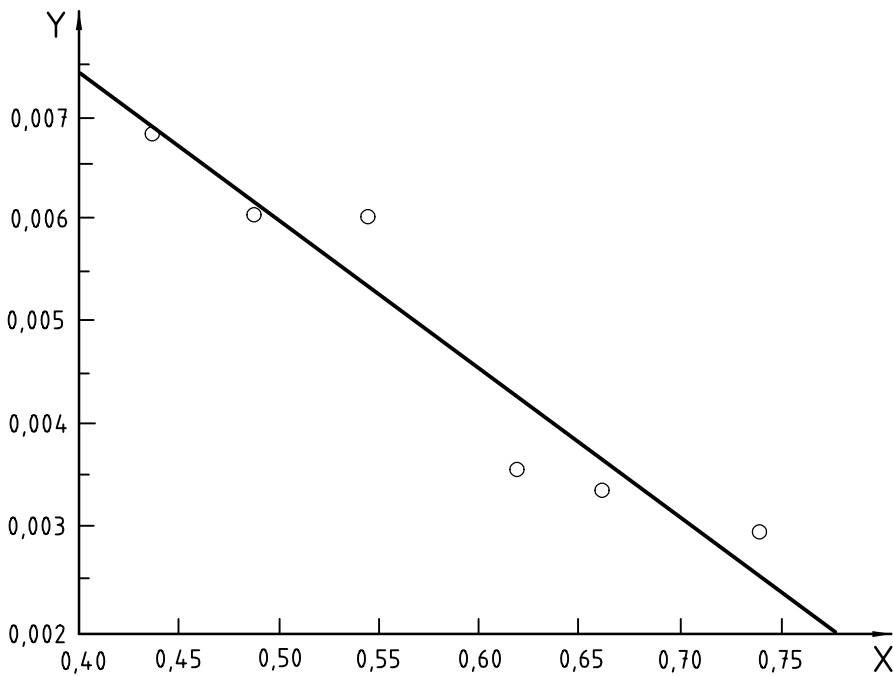
Key
 X log modulus
 Y log compliance
 $R^2 = 0,995$ No. of points = 24 $y = 2,28 - 1,84x$

Figure B.2 — Log compliance vs log modulus



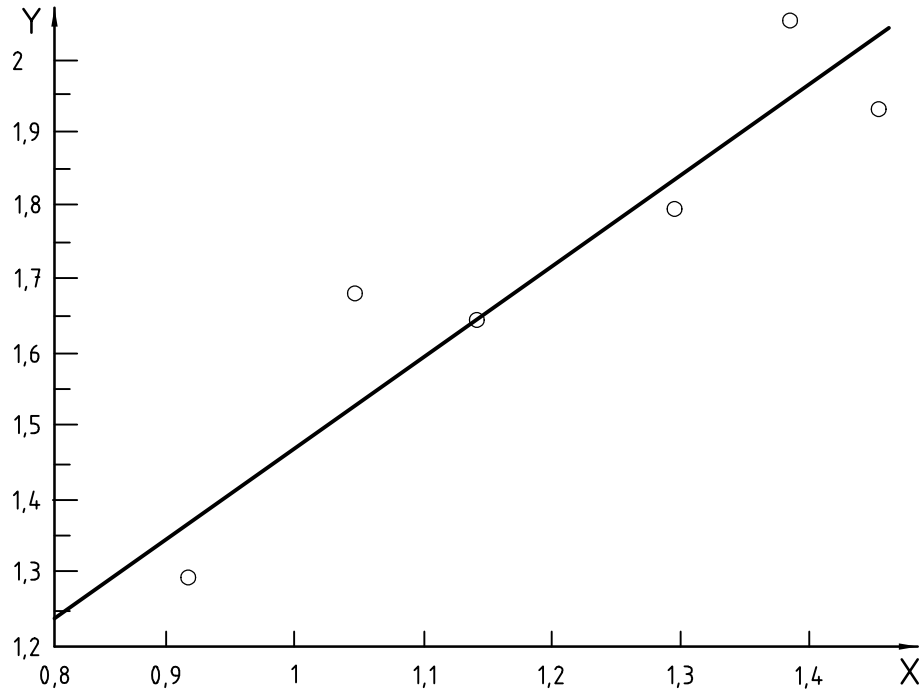
Key
 X log compliance
 Y standard deviation of log compliance
 $R^2 = 0,956$ No. of points = 6 $y = - 0,013 + 0,0176x$

Figure B.3 — Standard deviation of log compliance vs log compliance



Key
 X log modulus
 Y standard deviation of log modulus
 $R^2 = 0,912$ No. of points = 6 $y = 0,0132 - 0,0144x$

Figure B.4 — Standard deviation of log modulus vs log modulus



Key

X log compliance

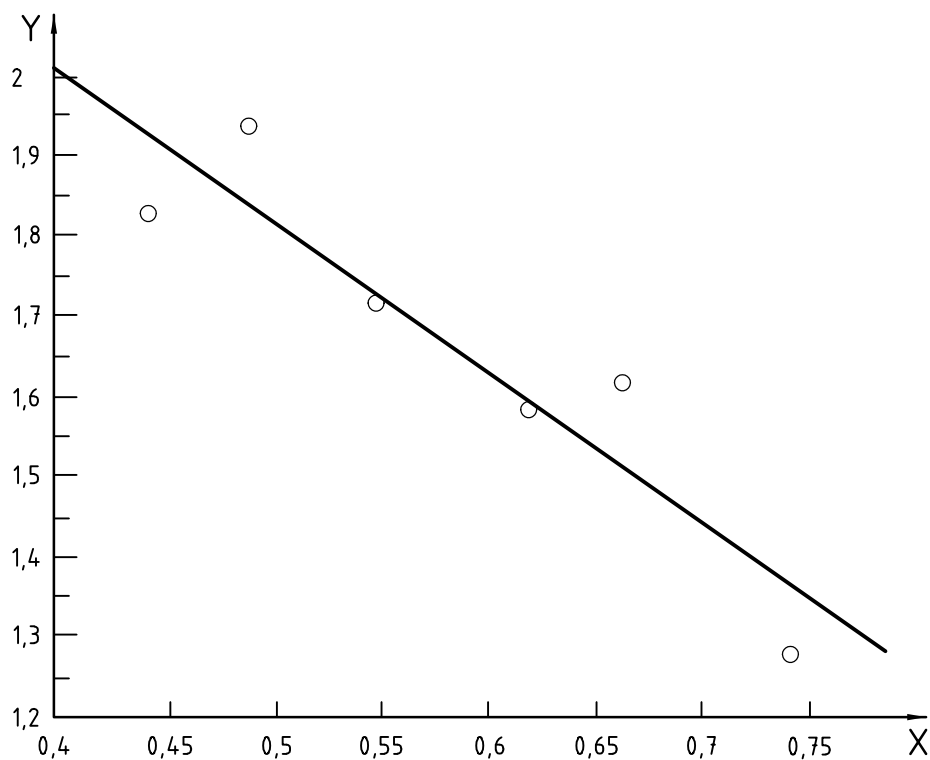
Y σ_1/σ_2

$R^2 = 0,859$

No. of points = 6

$y = 0,42 + 1,02x$

Figure B.5 — Ratio of standard deviation of log compliance to standard deviation of log modulus (σ_1/σ_2) vs log compliance



Key

X log modulus

Y σ_1/σ_2

$R^2 = 0,854$

No. of points = 6

$y = 2,76 - 1,89x$

Figure B.6 — Ratio of standard deviation of log compliance to standard deviation of log modulus (σ_1/σ_2) vs log modulus

Annex C (informative)

Background information on the transformation of plot scales and the derivation of the absolute sensitivity of a simple analytical test

C.1 Transformation of scales

C.1.1 The operation of transforming the scales of MP plots is important since it can be required to produce a linear relationship for MP_1 vs MP_2 . A linear relationship simplifies the determination of test sensitivity. This annex demonstrates that relative test sensitivity, ψ_R , is not changed by such a transformation of scale. If two test methods have different relationships as given by the equations:

$$MP_1 = f_1 \times FP \quad \text{and} \quad MP_2 = f_2 \times FP \quad (\text{C.1})$$

then ψ_R is given by Equation C.2 [i.e. Equation (6) in 5.3.3]:

$$\psi_R = \frac{\frac{\Delta(MP_1)}{\sigma_{MP1}}}{\frac{\Delta(MP_2)}{\sigma_{MP2}}} = \frac{|K_0| \times \sigma_{MP2}}{\sigma_{MP1}} \quad (\text{C.2})$$

The next step is the use of differentials rather than delta terms, thus:

$$\psi_{R(T1/T2)} = \frac{\frac{d(MP_1)}{\sigma_{MP1}}}{\frac{d(MP_2)}{\sigma_{MP2}}} = \frac{|K_0| \times \sigma_{MP2}}{\sigma_{MP1}} \quad (\text{C.3})$$

The T_1/T_2 notation is now included to avoid any confusion when comparing MP_1 vs MP_2 behaviour with MP_2 vs MP_3 behaviour as described below.

C.1.2 If there is a need to transform MP_1 for any reason, it can be indicated by another relationship as given by Equation (C.4):

$$MP_3 = f_3 \times MP_1 \quad (\text{C.4})$$

Then, by definition, the test sensitivity of MP_3 relative to MP_2 is given by:

$$\psi_{R(T3/T2)} = \frac{\frac{d(MP_3)}{\sigma_{MP3}}}{\frac{d(MP_2)}{\sigma_{MP2}}} = \frac{|K_0| \times \sigma_{MP2}}{\sigma_{MP3}} \quad (\text{C.5})$$

Since MP_1 is related to MP_2 , then MP_3 is also related to MP_2 and, by differentiating Equation (C.4) with respect to MP_2 , the following is obtained:

$$\frac{d(MP_3)}{d(MP_2)} = \frac{d(f_3 \times MP_1)}{d(MP_2)} \quad (\text{C.6})$$

Re-expressing the right-hand side of Equation (C.6), the equation becomes:

$$\frac{d(MP_3)}{d(MP_2)} = \frac{d(f_3 \times MP_3)}{d(MP_2)} = \frac{d(f_3 \times MP_1)}{d(MP_1)} \times \frac{d(MP_1)}{d(MP_2)} \quad (C.7)$$

From the law of propagation of errors, the relationship between the test errors in MP_3 and MP_1 is given by:

$$\sigma_{MP3} = \left| \frac{d(f_3 \times MP_1)}{d(MP_1)} \times \sigma_{MP1} \right| \quad (C.8)$$

Introducing Equations (C.7) and (C.8) into Equation (C.5) and using absolute values as indicated, $\psi_{R(T3/T2)}$ is defined by the ratio shown in Equation (C.9):

$$\psi_{R(T3/T2)} = \frac{\left| \frac{d(f_3 \times MP_1)}{d(MP_1)} \times \frac{d(MP_1)}{d(MP_2)} \right|}{\left| \frac{d(f_3 \times MP_1)}{d(MP_1)} \times \frac{\sigma_{MP1}}{\sigma_{MP2}} \right|} \quad (C.9)$$

which simplifies to:

$$\psi_{R(T3/T2)} = \frac{\left| \frac{d(MP_1)}{d(MP_2)} \right|}{\frac{\sigma_{MP1}}{\sigma_{MP2}}} \quad (C.10)$$

The ratio given in Equation (C.10) is the same as the ratio in the initial expression for the T_1/T_2 comparison given in Equation (C.3). The transformation of scale for MP_1 (to MP_3) has not changed the value of its relative sensitivity with respect to MP_2 . By the same reasoning, any transformation of MP_2 will give behaviour equivalent to that found for MP_1 . Thus the relative test sensitivity, ψ_R , is invariant with respect to scale transformations carried out on the measured property (MP) in either test method being compared.

C.1.3 Transforming the measured properties is usually a trial-and-error process. Typical transformations to produce linearity of the MP_1 vs MP_2 relationship are the use of the logarithm of either MP_1 or MP_2 or both, as well as the square root of either or both. Transformations also tend to reduce the perturbing influence of any non-normality in the underlying distributions for the measured properties as well as frequently stabilizing or equalizing the variance across the range of values for the reference materials.

C.2 Deriving the absolute sensitivity of a simple analytical test

C.2.1 In measurement techniques such as those employed in analytical chemistry, a material or constituent is determined by evaluating some quantity that is directly proportional to the amount of material or constituent present. As an example, in the "classic" analysis of total sulfur in rubber, the sulfur, after appropriate chemical reactions, is determined by the amount of barium sulfate precipitated. The discussion in this clause is devoted to a simple chemical test method for the quantitative analysis of one constituent. Under some circumstances, the procedure can also be applicable to simple physical tests.

C.2.2 Constituent A, a chemical element in some matrix of materials, is to be determined by reacting A (in a solution of the matrix materials) with a reagent to generate a carrier compound C, where the proportion of A in C is fixed by the stoichiometry of the chemical reaction. This carrier compound is determined by weighing, after separating it from the solution. The percentage of A, m_A , in the matrix of materials (the sample) is given by:

$$m_A = 100 \times \frac{m_C}{m_S} \times \frac{\{A\}}{\{C\}} \quad (C.11)$$

where

m_C is the mass of C as measured by the test method;

m_S is the mass of matrix (sample) used in the test method;

{A} is the equivalent mass of A in the chemical reaction which produces C;

{C} is the equivalent mass of C.

Equation (C.11) can be rewritten as:

$$m_A = 100R_M R_{EM} \quad (C.12)$$

where

$R_M = m_C/m_S$, the ratio of the measured mass of C to the mass of the sample;

$R_{EM} = \{A\}/\{C\}$, the ratio of the equivalent mass of A to the equivalent mass of C.

Based on Equation (C.12), the standard deviation for A can be expressed, in %, as:

$$\sigma_A = 100R_{EM}\sigma_{R_M} \quad (C.13)$$

where

σ_A is the standard deviation in determining A;

σ_{R_M} is the standard deviation in the measurement of R_M , i.e. m_C/m_S .

C.2.3 Equation (C.13) indicates that the precision in measuring A is improved when R_{EM} is small and the standard deviation in the measurement of R_M (ratio of mass of carrier compound C to mass of sample) is small.

Equation (C.12) can be rearranged to give R_M in terms of A:

$$R_M = \frac{m_A}{100R_{EM}} \quad \text{in \%} \quad (C.14)$$

Equation (C.14) shows that a plot of R_M (Y-axis) vs m_A (X-axis) is a straight line with zero intercept and a slope of $1/100R_{EM}$. If the slope is designated K , then $1/K = 100R_{EM}$ and Equation (C.13) can be written as:

$$\sigma_A = \frac{\sigma_{R_M}}{K} \quad \text{in \%} \quad (C.15)$$

Thus high precision for A is obtained when the ratio σ_{R_M}/K is small or, conversely, when K/σ_{R_M} is large. Since the sensitivity to the constituent being analysed is greater the higher the value of K/σ_{R_M} , this ratio is defined as the test sensitivity and is given by Equation (C.16), using absolute values (without regard to sign) of K :

$$\text{Absolute test sensitivity} = \psi_A = |K|/\sigma_{R_M} \quad (C.16)$$

Thus, although the technical merit of a test method requires that the measured property, in this case R_M , have a small standard deviation, it also requires a high rate of change in R_M with the rate or extent of change in A, i.e. it requires the ability to discriminate or readily detect small changes in A. The greater this detection capability or discrimination power, the greater is K . In the discussion in this annex, R_M is equal to MP and A is equal to FP, in relation to the terminology used in the main body of the standard.

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NOTE See also *Precision Measurement and Calibration — Statistical Concepts and Procedures*, Special Publication 300, Vol 1, National Bureau of Standards (1969) (The National Bureau of Standards is now the National Institute for Standards and Technology).

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