INTERNATIONAL STANDARD

ISO 19004

First edition
2004-10-01

Corrected version
2007-03-01

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

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

Reference number
ISO 19004:2004(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

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.

In this corrected version of ISO 19004:2004, the reference in the Bibliography to ASTM D 6600-00 has been transferred to Clause 1.

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.

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.

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

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.

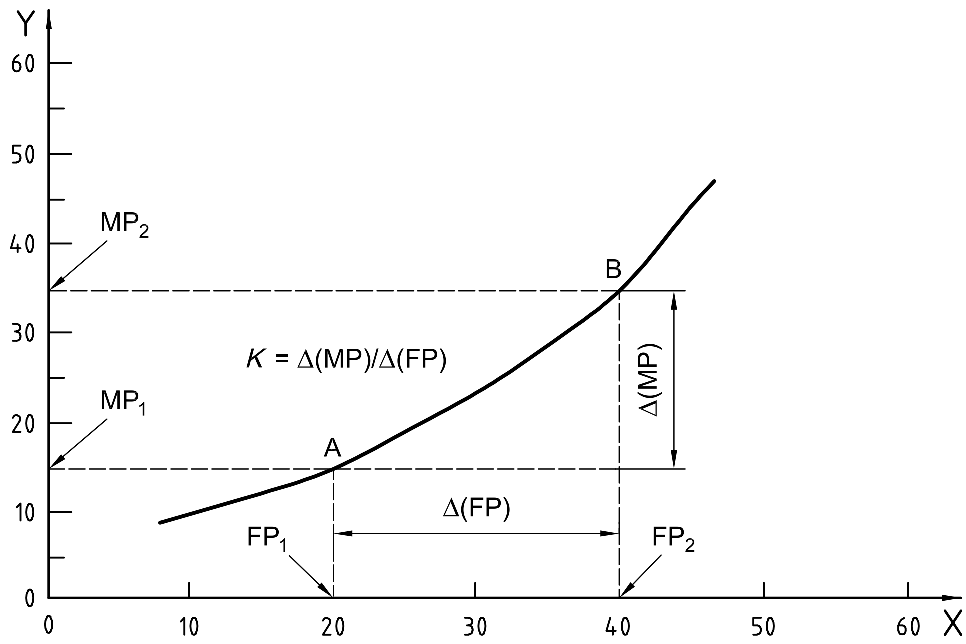
For global testing, an interlaboratory test programme (ITP) shall be conducted. Two or more replicate test sensitivity determinations shall be conducted in each participating laboratory, and an overall or average test sensitivity obtained across all the laboratories. In the context of an ITP for global 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 $K = \Delta(\mathrm{MP})/\Delta\,(\mathrm{FP})$. 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:

$$\psi_{\mathrm{A}} = \frac{|K|}{\sigma_{\mathrm{MP}}} \qquad (1)$$

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 $\mathrm{MP} = f \times \mathrm{FP}$ 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 Δ(MP) and Δ(FP) can be given in terms of differentials. When differentials are used, $K = |\mathrm{d(MP)/d(FP)}|$ 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.

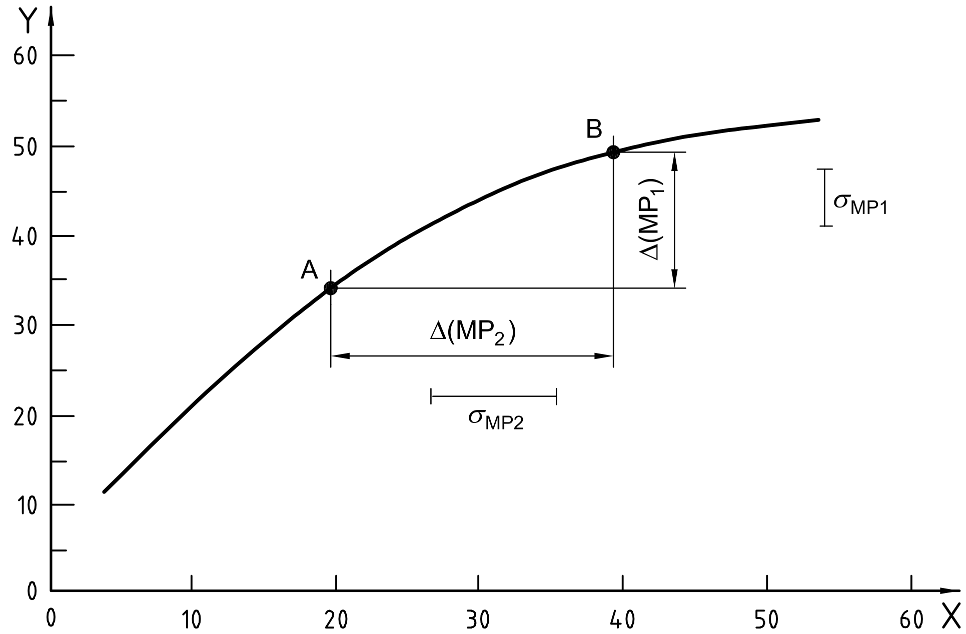
b) A theoretical evaluation, conducted using the known relationship between MP and FP, and based on scientific or theoretical principles, for a measurement system that permits the calculation of FP calibration values under certain specified conditions. This will not be addressed by this International 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 MP = $f \times$ 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 MP_2

Y measured property MP_1

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:

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

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 MP_1 and MP_2, 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

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

