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Rubber — Determination of metal content by atomic absorption spectrometry —

Part 3:
Determination of copper content

Caoutchouc — Détermination de la teneur en métal par spectrométrie d'absorption atomique —

Partie 3: Dosage du cuivre

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

This fourth edition cancels and replaces the third edition (ISO 6101-3:2014), which has been technically revised.

The main changes compared to the previous edition are as follows:

- in Clause 2, Clause 4 and 8.2.1, ISO 247 has been updated to ISO 247-1;
- in Clause 4, 6.3 and 8.2.1, the ashing temperature for rubber products (950 °C) has been added;
- in 5.2, the concentration of dilute hydrochloric acid has been reduced to 2 %;
- in 5.8, the amount of nitric acid to prepare 1,6 % dilute nitric acid has been changed from 11,5 cm^3 to 16 cm^3 to correct a calculation error;
- in 5.10, 8.2.2, 8.3.1.1, 8.4.2 and 8.5, the concentration of hydrochloric acid in the standard solution, the sample solution and the calibration solutions has been changed to about 2 % to prevent the burner from getting dirty or damage (in the alternative method given in 8.2.3, the concentration of nitric acid in these solutions is 1,6 %);
- in 8.2.1, 8.2.2 and 8.2.3, the sentence “moisten the ash with some drops of water, then add HCl/HNO_3 acid” has been added and the sentence “stir carefully with the platinum or borosilicate-glass rod” has been deleted to avoid ash losses;
- in 8.2.2, the dissolution of inorganic residue process has been aligned with 8.2.3 to account for the reduced concentration of the dilute hydrochloric.

A list of all parts in the ISO 6101 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Rubber — Determination of metal content by atomic absorption spectrometry —

Part 3:
Determination of copper content

WARNING 1 — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine applicability of any national regulatory conditions.

WARNING 2 — Certain procedures specified in this document can involve the use or generation of substances, or the generation of waste, that can constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This document specifies an atomic absorption spectrometric method for the determination of the copper content of rubbers.

The method is applicable to raw rubber and rubber products having copper contents above 1 ppm. Copper contents below this limit can be determined, provided that suitable adjustments are made to either the mass of the test portion or to the concentrations of the solutions used, or both. The use of the standard additions method can lower the bottom limit of detection.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 123, *Rubber latex — Sampling*

ISO 124, *Latex, rubber — Determination of total solids content*

ISO 247-1, *Rubber — Determination of ash — Part 1: Combustion method*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 835, *Laboratory glassware — Graduated pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 1772, *Laboratory crucibles in porcelain and silica*

ISO 1795, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

4 Principle

A test portion is ashed at 550 °C ± 25 °C for raw natural rubber or at 950 °C ± 25 °C for rubber products having high carbon black content in accordance with ISO 247-1. The ash is dissolved in hydrochloric acid or nitric acid. The solution is aspirated into an atomic absorption spectrometer and the absorption is measured at a wavelength of 324,7 nm, using a copper hollow-cathode lamp as the copper emission source. Any silicates are volatilized by sulfuric and hydrofluoric acid.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

5.1 Hydrochloric acid, ρ_{20} = 1,18 Mg/m^3, a mass fraction of 37 %.

5.2 Dilute hydrochloric acid, a mass fraction of 2 %, prepared by adding 64 cm^3 of concentrated hydrochloric acid (5.1) into a 1 000 cm^3 one-mark volumetric flask, making up to the mark with water and mixing thoroughly.

5.3 Sulfuric acid, ρ_{20} = 1,84 Mg/m^3, a mass fraction of 95 % to a mass fraction of 97 %.

5.4 Sulfuric acid, diluted 1 + 3, add carefully 1 volume of concentrated sulfuric acid (5.3) to 3 volumes of water.

5.5 Hydrofluoric acid, ρ_{20} = 1,13 Mg/m^3, a mass fraction of 38 % to a mass fraction of 40 %.

5.6 Hydrogen peroxide solution, with a mass fraction of 30 %.

5.7 Concentrated nitric acid, ρ_{20} = 1,41 Mg/m^3, a mass fraction of 65 % to a mass fraction of 70 %.

5.8 Dilute nitric acid, a mass fraction of 1,6 %, prepared by adding 16 cm^3 of concentrated nitric acid (5.7) into a 1 000 cm^3 one-mark volumetric flask, making up to the mark with water and mixing thoroughly.

5.9 Standard copper stock solution, containing 1,0 g of Cu per 1 000 cm^3.

Either use a commercially available standard copper solution, or prepare as follows: weigh, to the nearest 0,1 mg, 1 g of electrolytic copper (purity ≥ 99,9 %) and dissolve in 50 cm^3 of concentrated hydrochloric acid (5.1). Add 15 cm^3 of hydrogen peroxide solution (5.6). After dissolution, decompose the excess hydrogen peroxide by boiling. Allow to cool and transfer quantitatively to a 1 000 cm^3 one-mark volumetric flask (6.5). Dilute to the mark and mix thoroughly.

1 cm^3 of this standard stock solution contains 1 000 µg of Cu.

5.10 Standard copper solution, containing 10,0 mg of Cu per 1 000 cm^3.

Carefully pipette 10,0 cm^3 of the standard copper stock solution (5.9) into a 1 000 cm^3 one-mark volumetric flask (6.5) and dilute to the mark with dilute hydrochloric acid (5.2) or dilute nitric acid (5.8) and mix thoroughly. Prepare this solution on the day of use.

1 cm^3 of this standard stock solution contains 10 µg of Cu.

6 Apparatus

Ordinary laboratory apparatus, plus the following.

6.1 Atomic absorption spectrometer, fitted with a burner fed with acetylene and air, compressed to at least 60 kPa and 300 kPa, respectively, and also fitted with a copper hollow-cathode lamp as the copper emission source.

The instrument shall be operated in accordance with the manufacturer's instructions for optimum performance.

Alternatively, an electrothermal atomization device (graphite furnace) may be used. It shall be operated by a competent person in accordance with the manufacturer's instructions for optimum performance.

6.2 Balance, accurate to 0,1 mg.

6.3 Muffle furnace, capable of being maintained at a temperature of (550 ± 25) °C or (950 ± 25) °C.

6.4 Glass filter crucible, filter pore size 16 µm to 40 µm (porosity grade P40 according to ISO 4793).

6.5 One-mark volumetric flasks, glass-stoppered, of capacities 50 cm^3, 100 cm^3, 200 cm^3, 500 cm^3 and 1 000 cm^3, complying with the requirements of ISO 1042:1998, class A.

6.6 Volumetric pipettes, of capacities 5 cm^3, 10 cm^3, 20 cm^3, and 50 cm^3, complying with the requirements of ISO 648:2008, class A.

6.7 Graduated pipette, of capacity 1 cm^3, complying with the requirements of ISO 835:2007, class A.

6.8 Electric hotplate or **heated sand bath**.

6.9 Platinum or **borosilicate-glass rod**, for use as a stirrer.

6.10 Crucible (platinum), of capacity 50 cm^3 to 150 cm^3 depending on the test portion size.

6.11 Crucible (silica, porcelain, or borosilicate glass), of capacity 50 cm^3 to 150 cm^3 depending on the test portion size, complying with the requirements of ISO 1772.

6.12 Ashless filter paper.

7 Sampling

Carry out sampling as follows:

- raw rubber: in accordance with ISO 1795;
- latex: in accordance with ISO 123;
- products: to be representative of the whole batch.

8 Procedure

8.1 Test portion

Weigh, to the nearest 0,1 mg, approximately 1 g to 5 g of rubber product, or 5 g to 10 g of raw rubber, milled or finely cut, into an appropriate crucible. Wrap the test portion in an ashless filter paper and place into an appropriate crucible (6.10 or 6.11). The size of the test portion shall be judged by prior knowledge of the approximate amount of copper present.

For natural rubber latex concentrate, take a portion of thoroughly mixed latex containing about 20 g of total solids, make into a thin film by pouring the portion onto a glass plate, dry to constant mass as specified in ISO 124 and cut into small pieces.

For raw, natural rubber, take the test portion from a test sample prepared in accordance with ISO 1795.

8.2 Preparation of test solution

8.2.1 Destruction of organic matter

Ash the test portion in accordance with ISO 247-1, in the muffle furnace (6.3), maintained at 550 °C ± 25 °C for raw natural rubber or at 950 °C ± 25 °C for rubber products. After ashing, allow the crucible and its contents to cool to ambient temperature.

If the ash is black, caused by small amounts of carbon black, moisten the ash by carefully adding some drops of water then add 1 cm^3 of concentrated nitric acid (5.7) to the ash, evaporate to dryness on an electrical heating plate or sand bath (6.8) and return to the muffle furnace and ash for 10 min to 15 min.

8.2.2 Dissolution of inorganic residue using hydrochloric acid

After ashing, allow the crucible and its contents to cool to ambient temperature. Add a few drops of distilled water to moisten the ash, and then add 10 cm^3 of dilute hydrochloric acid (5.2). Cover with watch glass and heat the mixture on the electric hotplate or heated sand bath (6.8) for at least 30 min. Do not let the reaction mixture boil. Allow to cool to ambient temperature. Filter the contents of the crucible into a 50 cm^3 one-mark volumetric flask (6.5), rinsing the crucible and filling it up to the mark with dilute hydrochloric acid (5.2). If the ash is not totally dissolved, proceed as follows.

— Transfer the solution and the undissolved ash quantitatively, with the aid of water, to a platinum crucible (6.11). Add a few drops of concentrated sulfuric acid (5.3) and 5 cm^3 of hydrofluoric acid (5.5). Heat on the electric hotplate or heated sand bath (6.8) in a fume cupboard and evaporate to dryness, while stirring with a platinum rod (6.9). Repeat this digestion with the same quantities of sulfuric and hydrofluoric acids two more times.

— Allow to cool to ambient temperature, moisten the ash with some drops of water then add 10 cm^3 of dilute hydrochloric acid (5.2), heat for 30 min. Allow to cool to ambient temperature. Filter the contents of the crucible into a 50 cm^3 one-mark volumetric flask (6.5), rinsing the crucible and filling it up to the mark with dilute hydrochloric acid (5.2).

8.2.3 Dissolution of inorganic residue using nitric acid — Alternative method

Add a few drops of distilled water to moisten the ash and then add 10 cm^3 of dilute nitric acid (5.8) to the cooled residue. Cover with a watch glass and heat on an electric hotplate or heated sand bath (6.8) for at least 30 min. Allow to cool to ambient temperature. Filter the contents of the crucible into a 50 cm^3 one-mark volumetric flask, rinsing the crucible, and filling it up to the mark with dilute nitric acid (5.8).

8.3 Preparation of the calibration graph

8.3.1 Preparation of calibration solutions

8.3.1.1 Into a series of five 100 cm^3 one-mark volumetric flasks (6.5), introduce, using pipettes (6.6) the volumes of standard copper solution (5.10) indicated in Table 1. Dilute to the mark with dilute hydrochloric acid solution (5.2) or dilute nitric acid (5.8) and mix thoroughly.

Table 1 — Standard calibration solutions

Volume of standard copper solution cm^3	Mass of copper contained in 1 cm^3 µg
50,0	5,0
20,0	2,0
10,0	1,0
5,0	0,5
0	0

8.3.1.2 Prepare the set of calibration solutions immediately prior to the determination.

8.3.2 Spectrometric measurements of calibration solutions

Switch on the spectrometer (6.1) sufficiently in advance to ensure stabilization. With the copper hollow-cathode tube suitably positioned, adjust the wavelength to 324,7 nm and the sensitivity and slit aperture according to the characteristics of the instrument.

Adjust the pressures and flow rates of the air and of the acetylene in accordance with the manufacturer's instructions to obtain a clear blue, non-luminous, oxidizing flame, suited to the characteristics of the particular spectrometer being used.

Aspirate the set of calibration solutions in succession into the flame and measure the absorbance of each solution twice, averaging the readings. Take care that the aspiration rate is constant throughout this process. Ensure also that at least one calibration solution is at or below the analyte level found in the rubber being tested.

Aspirate water through the burner after each measurement.

8.3.3 Plotting the calibration graph

Plot a graph having, for example, the masses, in micrograms, of copper contained in 1 cm^3 of the calibration solutions as abscissae and the corresponding values of absorbance, corrected for the absorbance of the calibration blank, as ordinates. Represent the points on the graph by the best straight line as judged visually or as calculated by the least-squares fit method.

8.4 Determination

8.4.1 Spectrometric measurements of test solution

Carry out duplicate spectrometric measurements at a wavelength of 324,7 nm on the test solution prepared in 8.2.2 or 8.2.3, following the procedure specified in 8.3.2.

8.4.2 Dilution

If the instrument response for the test solution is greater than that found for the calibration solution having the highest copper content, dilute, as appropriate, with dilute hydrochloric acid solution (5.2) or dilute nitric acid (5.8) in accordance with the following procedure.

Pipette carefully a suitable volume V (cm^3) of the test solution into a 100 cm^3 one-mark volumetric flask (6.5) so that the copper concentration lies within the range covered by the calibration solutions. Dilute to the mark with dilute hydrochloric acid (5.2) or dilute nitric acid (5.8). Repeat the spectrometric measurements.

NOTE To increase the reliability of the test method, the standard-additions method can be used (see Annex A).

8.5 Blank determination

Carry out a blank test in parallel with the determination, using dilute hydrochloric acid (5.2) or dilute nitric acid (5.8), but omitting the test portion.

If the preparation of the test solution involved the use of sulfuric acid and hydrofluoric acid, prepare the blank test solution by repeating that procedure, but omitting the test portion.

8.6 Number of determinations

Carry out the procedure in duplicate, using separate test portions cut from the same homogenized sample.

9 Expression of results

9.1 Read the copper content of the test solution directly from the calibration graph plotted in 8.3.3. The copper content of the test portion, expressed as a percentage mass fraction, is given by Formula (1):

$$\frac{\rho(Cu)_\mathrm{t} - \rho(Cu)_\mathrm{b}}{200m} \times f \tag{1}$$

where

$\rho(\mathrm{Cu})_\mathrm{t}$ is the copper content, in micrograms per cubic centimetre, of the test solution, read from the calibration graph;

$\rho(\mathrm{Cu})_\mathrm{b}$ is the copper content, in micrograms per cubic centimetre, of the blank test solution, read from the calibration graph;

m is the mass, in grams, of the test portion;

f is the test solution dilution factor, if required (see 8.4.2), given by: $f = \frac{100}{V}$ where V is the volume, in cubic centimetre, of test solution taken in 8.4.2.

9.2 The copper content of the test portion can also be calculated, in micrograms per cubic centimetre, of the test solution, by Formula (2):

$$\frac{\rho(Cu)_\mathrm{t} - \rho(Cu)_\mathrm{b}}{200m} \times f \tag{2}$$

where

$\rho(\mathrm{Cu})_\mathrm{t}$ is the copper content, in micrograms per cubic centimetre, of the test solution, given by Formula (3):

$$\rho(Cu)_\mathrm{t} = \frac{A_\mathrm{t} \times \rho(Cu)_\mathrm{n}}{A_\mathrm{n}} \tag{3}$$

$\rho(\mathrm{Cu})_\mathrm{b}$ is the copper content, in micrograms per cubic centimetre, of the blank test solution, given by Formula (4):

$$\rho(Cu)_\mathrm{b} = \frac{A_\mathrm{b} \times \rho(Cu)_\mathrm{n}}{A_\mathrm{n}} \tag{4}$$

where

A_t is the absorbance of the test solution;

A_b is the absorbance of the blank test solution;

A_n is the absorbance of the standard calibration solution having the copper content closest to that of the test solution;

$\rho(\mathrm{Cu})_\mathrm{n}$ is the copper content, in micrograms per cubic centimetre, of the standard calibration solution having the absorbance closest to that of the test solution;

m is the mass, in grams, of the test portion;

f is the test solution dilution factor, if required (see 8.4.2), given by: $f = \frac{100}{V}$ where V is the volume, in cubic centimetre, of test solution taken in 8.4.2.

9.3 The test result is the average of two determinations, rounded to two decimal places when the copper concentration is expressed as a percentage and to the nearest whole number when the concentration is expressed in milligrams per kilogram.

9.4 Report the copper content as a percentage if greater than or equal to 0,1 % or as milligrams per kilogram if less than 0,1 %.

10 Precision

See Annex B.

11 Test report

The test report shall include the following information:

a) a reference to this document (i.e. ISO 6101-3:2022);

b) all details necessary for the complete identification of the product tested;

c) the method of sampling used;

d) the type of instrument used (flame or graphite furnace spectrometer);

e) the results obtained and the units in which they have been expressed;

f) any unusual features noted during the determination;

g) any operations not included in this document, or in the International Standards to which reference is made, as well as any incident which can have affected the results.

h) the date of the test.

Annex A
(informative)

Method of standard additions

The method of standard additions provides the analyst with a powerful tool for increasing the accuracy of an atomic absorption analysis.

It is used either with samples containing unknown concentrations of matrix materials, with samples which are difficult to duplicate with blanks or when it is necessary to lower the limits of detection, or all.

The method of standard additions can be found in any standard textbook on atomic absorption and is usually described in the user's manual supplied with the atomic absorption spectrometer.

The following example illustrates the method.

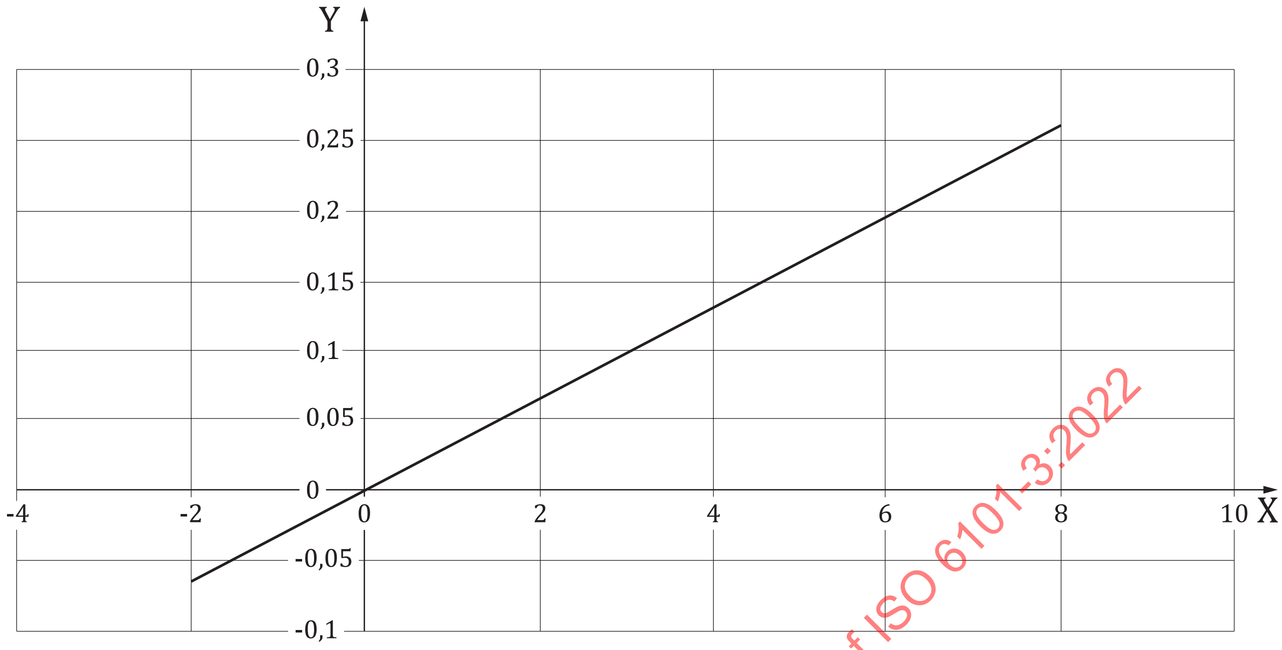
— From a test solution prepared as described in 8.2, take four aliquots of the same size. To three of these aliquots, add a different, but known volume of standard copper solution. Make up the volumes to the same total for all four aliquots. Use concentrations which fall on the linear portion of the calibration graph.

— Measure the absorbance of each of the four solutions so obtained.

— Plot the absorbance on the Y-axis and the concentration, in micrograms of copper per cubic centimetre of solution, on the X-axis.

— Extrapolate the straight line to intersect the X-axis (zero absorbance). At the point of intersection with the Y-axis, read the concentration of copper in the test solution.

An example is given in Figure A.1.



Key

X concentration of copper in solution, µg/cm^3

Y absorbance

Figure A.1 — Example of a graph obtained using the method of standard additions

Annex B
(informative)

Precision

B.1 General

The precision of the test method was determined in accordance with ISO/TR 9272, which has now been withdrawn and replaced with ISO 19983, which can be referred to for terminology and other statistical details.

The precision data are given in Table B.1. The precision parameters should not be used for acceptance or rejection of any group of materials without documentation that the parameters are applicable to those particular materials and specific test protocols of the test method. The precision is expressed on the basis of a 95 % confidence level for the values established for repeatability, r, and reproducibility, R.

The results contained in Table B.1 are average values and give an estimate of the precision of this test method as determined in an interlaboratory test programme, carried out in 2012, in which seven laboratories took part, performing duplicate analyses on two samples, A and B, prepared from high-ammonia natural rubber latex concentrate. Before the bulk latex was sub-sampled into two bottles labelled A and B, it was filtered and homogenized by thorough stirring. Thus, essentially, samples A and B were the same and were treated as such in the statistical computations. Each participating laboratory was required to carry out the test, using these two samples, on the dates given to them.

A type 1 precision was evaluated, based on the method of sampling used for the interlaboratory test programme.

B.2 Repeatability

The repeatability r, in measurement units, of the test method has been established as the appropriate value tabulated in Table B.1. Two single test results, obtained in the same laboratory under normal test method procedures, that differ by more than the tabulated value of r (for any given level) should be considered to have come from different or non-identical sample populations.

B.3 Reproducibility

The reproducibility R, in measurement units, of the test method has been established as the appropriate value tabulated in Table B.1. Two single test results, obtained in different laboratories under normal test method procedures, that differ by more than the tabulated value of R (for any given level) should be considered to have come from different or non-identical sample populations.

B.4 Bias

In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values do not exist for this test method since the value (of the test property) is exclusively defined by the test method. Bias cannot therefore be determined for this particular method.