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Steel and cast iron — Determination of copper content — Flame atomic absorption spectrometric method

Aciers et fontes — Détermination de la teneur en cuivre — Méthode par spectrométrie d'absorption atomique dans la flamme

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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).

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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 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 459/SC 2, *Methods of chemical analysis for iron and steel*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 4943:1985), which has been technically revised. The main changes are as follows:

- extension of the determination range;
- re-organization of a precision test;
- re-assessment of the precision data.

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.

Steel and cast iron — Determination of copper content — Flame atomic absorption spectrometric method

1 Scope

This document specifies a flame atomic absorption spectrometric method for the determination of copper in steel and cast iron.

The method is applicable to copper contents in the range of 0,003 % (mass fraction) to 3,0 % (mass fraction).

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 648, *Laboratory glassware — Single-volume pipettes*

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

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 14284, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*

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

Dissolution of a test portion in a mixture of hydrochloric, nitric and perchloric acids.

Nebulization of the test solution into an air/acetylene flame of an atomic absorption spectrometer. Spectrometric measurement of the atomic absorption of the 324,7 nm or 327,4 nm spectral line emitted by a copper hollow-cathode lamp.

NOTE Other suitable radiation sources can also be used.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only grade 2 water as specified in ISO 3696.

5.1 Pure iron, containing less than 0,000 5 % (mass fraction) of copper or having a very low and known copper content.

5.2 Hydrochloric acid-nitric acid mixture.

Mix three parts by volume of hydrochloric acid (ρ about 1,19 g/ml), one part by volume of nitric acid (ρ about 1,40 g/ml), and two parts by volume of water.

Prepare this mixture immediately before use.

5.3 Hydrochloric, nitric and perchloric acids mixture.

Mix 20 ml of hydrochloric acid (ρ about 1,19 g/ml) with 55 ml of nitric acid (ρ about 1,40 g/ml) and 75 ml of perchloric acid (ρ about 1,54 g/ml).

NOTE Perchloric acid (ρ about 1,67 g/ml) can also be used. 100 ml of perchloric acid (ρ about 1,54 g/ml) are equivalent to 79 ml of perchloric acid (ρ about 1,67 g/ml).

5.4 Copper standard solution, 1,0 g/l.

Weigh (1,000 ± 0,001) g of copper [purity >99,95 % (mass fraction)]. Transfer into a 400 ml beaker, add 25 ml of nitric acid (ρ about 1,40 g/ml, diluted 1 + 4) and cover with a watch-glass. Heat gently to complete dissolution. Allow to cool, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 1 mg of Cu.

5.5 Copper standard solution, 20 mg/l.

Transfer 20,0 ml of the standard solution (5.4) into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 20 µg of Cu.

Prepare this standard solution immediately before use.

6 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 648 or ISO 1042 as appropriate.

All glassware shall first be washed in hydrochloric acid (ρ about 1,19 g/ml, diluted 1 + 1), and then in water. The quantity of copper present in the beakers and flasks can be checked by measuring the absorption of distilled water introduced in the glassware after the acid wash.

Ordinary laboratory apparatus and the following shall be used.

6.1 Atomic absorption spectrometer

The spectrometer shall be equipped with a copper hollow-cathode lamp, and supplied with air and acetylene sufficiently pure to give a steady clear fuel-lean flame, free from water and oil, and free from copper.

NOTE Other suitable radiation sources can also be used.

The atomic absorption spectrometer used will be satisfactory if, after optimization in accordance with 8.3.4, the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and it meets the precision criteria given in 6.1.1 to 6.1.3.

The instrument should also conform to the additional performance requirement given in 6.1.4.

6.1.1 Minimum precision

Use the procedures described in Annex A. Calculate the standard deviation of 10 measurements of the absorbance of the most concentrated calibration solution. This standard deviation shall not exceed 1,0 % of the mean absorbance.

Calculate the standard deviation of 10 measurements of the absorbance of the least concentrated calibration solution (excluding the zero member). This standard deviation shall not exceed 0,5 % of the mean absorbance of the most concentrated calibration solution.

6.1.2 Limit of detection

Use the procedures described in Annex A. The limit of detection is a number, expressed in units of concentration (or amount) that describes the lowest concentration level (or amount) of an element that can be determined to be statistically different from an analytical blank.

The limit of detection of copper in a matrix similar to the final test portion solution shall be better than 0,05 µg/ml.

6.1.3 Calibration linearity

Use the procedures described in Annex A. The slope of the calibration curve covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 times the value of the slope for the bottom 20 % of the concentration range (expressed as a change in absorbance) determined in the same way.

For instruments with automatic calibration using two or more standards, it shall be established prior to the analysis, by obtaining absorbance readings, that the above requirements for graph linearity are fulfilled.

6.1.4 Characteristic concentration

Use the procedures described in Annex A. The characteristic concentration for copper in a matrix similar to the final test portion solution shall be better than 0,08 µg/ml for 324,7 nm.

6.2 Ancillary equipment

Scale expansion can be used until the noise observed is greater than the read-out error and is always recommended for absorbances below 0,1. If scale expansion must be used and the instrument does not have the means to read the value of the scale expansion factor, the value can be calculated by measuring a suitable solution with and without scale expansion and then dividing the signal obtained.

7 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steel and cast iron.

8 Procedure

WARNING — Perchloric acid vapour can cause explosions in the presence of ammonia, nitrous fumes or organic matter in general. All evaporations shall be carried out in fume cupboards suitable for use with perchloric acid.

Ensure that the spray system and drainage system are washed free from perchloric acid after use.

8.1 Test portion

Weigh, to the nearest 0,001 g, approximately 0,50 g of the test sample.

8.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all the reagents, including pure iron (5.1) instead of the test portion.

8.3 Determination

8.3.1 Preparation of the test solution

8.3.1.1 Dissolution of the test portion

Place the test portion (8.1) in a 250 ml beaker. Add, in small portions, 20 ml of the acid mixture (5.3) for samples not readily soluble in the acid mixture (5.3), first dissolve in 10 ml of the acid mixture (5.2) before adding 20 ml of the acid mixture (5.3), cover the beaker with a watch-glass and heat gently until the acid action ceases. Evaporate until dense white fumes of perchloric acid appear. Continue fuming at a suitable temperature to maintain a steady reflux of white perchloric acid fumes on the walls of the beaker until salts crystallization.

Allow to cool, add 25 ml of water and heat gently to dissolve the salts. Cool again and transfer the test solution quantitatively into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Filter by decantation through a dry medium texture filter paper to remove any residue or precipitate, for example graphite, silica or tungstic acid, and collect the filtrate in a dry beaker after discarding the first portions.

8.3.1.2 Dilution of the test solution

Depending on the copper content expected in the test portion, prepare the test solution in accordance with a), b), or c), as follows:

a) If the expected copper content is up to 0,1 % (mass fraction), use the filtrate (see 8.3.1.1) undiluted.

b) If the expected copper content is between 0,1 % (mass fraction) and 1,0 % (mass fraction), transfer 10,0 ml of the test solution into a 100 ml one-mark volumetric flask, dilute to the mark with water and mix.

c) If the expected copper content is between 1,0 % (mass fraction) and 3,0 % (mass fraction), transfer 5,0 ml of the test solution into a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

In the cases where the test solution must be diluted, the blank test (8.2) shall be diluted in the same way.

8.3.2 Preparation of the calibration solutions

8.3.2.1 Dissolution of the pure iron

Place (5,00 ± 0,01) g of the pure iron (5.1) in a 500 ml beaker. Add in small portions 200 ml of the acid mixture (5.3) and heat gently until the dissolution is achieved.

Evaporate until dense white fumes of perchloric acid appear. Continue fuming at a suitable temperature to maintain a steady reflux of white perchloric acid fumes on the walls of the beaker until salts crystallization.

Allow to cool, add 100 ml of water and heat gently to dissolve the salts. Cool again and transfer the solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix.

8.3.2.2 Copper contents up to 0,1 % (mass fraction)

Transfer into a series of 100 ml one-mark volumetric flasks 50,0 ml of the iron solution (8.3.2). Using a burette or pipette, add the volumes of the copper standard solution (5.5) given in Table 1. Dilute to the mark with water and mix.

Table 1 — Calibration solutions for copper contents up to 0,1 % (mass fraction)

Volume of copper standard solution (5.5) ml	Mass of copper mg	Corresponding content of copper in the test sample % (mass fraction)
0[a]	0	0
0,5	0,01	0,002
2,5	0,05	0,010
5,0	0,10	0,020
10,0	0,20	0,040
15,0	0,30	0,060
20,0	0,40	0,080
25,0	0,50	0,100

[a] Zero member.

8.3.2.3 Copper contents between 0,1 % (mass fraction) and 1,0 % (mass fraction)

Transfer into a series of 100 ml one-mark volumetric flasks 5,0 ml of the iron solution (8.3.2). Using a burette or pipette, add the volumes of the copper standard solution (5.5) given in Table 2. Dilute to the mark with water and mix.

Table 2 — Calibration solutions for copper contents between 0,1 % (mass fraction) and 1,0 % (mass fraction)

Volume of copper standard solution (5.5) ml	Mass of copper mg	Corresponding content of copper in the test sample % (mass fraction)
0[a]	0	0
2,5	0,05	0,10
5,0	0,10	0,20
10,0	0,20	0,40
15,0	0,30	0,60
20,0	0,40	0,80
25,0	0,50	1,00

[a] Zero member.

8.3.2.4 Copper contents between 1,0 % (mass fraction) and 3,0 % (mass fraction)

Transfer into a series of 100 ml one-mark volumetric flasks 1,0 ml of the iron solution (8.3.2). Using a burette or pipette, add the volumes of the copper standard solution (5.5) given in Table 3. Dilute to the mark with water and mix.

Table 3 — Calibration solutions for copper contents between 1,0 % (mass fraction) and 3,0 % (mass fraction)

Volume of copper standard solution (5.5) ml	Mass of copper mg	Corresponding content of copper in the test sample % (mass fraction)
0[a]	0	0
5,0	0,10	1,0
7,5	0,15	1,5
10,0	0,20	2,0
12,5	0,25	2,5
15,0	0,30	3,0

[a] Zero member.

8.3.3 Adjustment and optimization of atomic absorption spectrometer

Fit the copper hollow-cathode lamp (see 6.1) to the atomic absorption spectrometer (6.1), switch on the current and allow it to stabilize.

Adjust the wavelength at 324,7 nm for copper contents within the whole range or at 327,4 nm for copper contents between 0,1 % to 3,0 % (mass fractions) to minimum absorbance, if possible.

Following the manufacturer's instructions, fit an air/acetylene burner, light the flame, and allow the burner temperature to stabilize.

Set the absorbance value at zero using zero member (8.3.2.1, 8.3.2.2 or 8.3.2.3).

Choose a damping setting or integration time to give a signal steady enough to fulfil the precision criteria given in 6.1.1 to 6.1.4.

Taking careful note of the manufacturer's instructions regarding the minimum flow rate of acetylene, nebulize alternately the calibration solution of highest concentration and the zero member, adjust the gas flow and burner position (horizontally, vertically and rotationally) until the difference in absorbance between the calibration solutions is at a maximum.

NOTE Other suitable radiation sources can also be used.

WARNING — The manufacturer's recommendations shall be closely followed and particular attention is drawn to the following safety points:

a) the explosive nature of acetylene, and regulations concerning its use;

b) the need to shield the eyes of the operator from ultraviolet radiation by means of tinted glass;

c) the need to keep the burner head clear of deposits because a badly clogged burner can cause a flashback;

d) the need to ensure that the liquid trap is filled with water;

e) the need to always spray water between the test solutions, blank solution and/or calibration solutions.

Evaluate the criteria of 6.1.1 to 6.1.3 and additional performance requirement of 6.1.4 to ensure that the instrument is suitable for the determination.

8.3.4 Spectrometric measurements

8.3.4.1 Spectrometric measurement of the calibration solutions

Nebulize the relevant series of calibration solutions (8.3.2.1 or 8.3.2.2 or 8.3.2.3) depending on the expected copper content in succession into the flame and measure the absorbance for each solution. Take care to keep the aspiration rate constant throughout the preparation of the calibration curve. Spray water through the burner after each measurement.

NOTE For certain types of apparatus, a solution containing the attack reagents can be used in the same concentrations as in the test solutions, instead of water.

8.3.4.2 Spectrometric measurement of the test solutions

Measure the absorbance of the blank test solution (8.2) and repeat the measurements of the test solution (8.3.1). Nebulize calibration solutions at frequent intervals during the measurement of a batch of determinations.

8.4 Plotting the calibration curve

Prepare a new calibration graph for each series of determinations and for each range of copper contents.

Use an appropriate spectrometer software or an off-line computer for regression calculations or prepare a graphical representation.

Obtain the net absorbance of each calibration solution by subtracting the absorbance of the zero calibration solution (zero member).

Prepare a calibration graph by plotting the net absorbance values of the calibration solution against the concentration of copper, expressed in micrograms per millilitre.

9 Expression of results

Convert the absorbances of the test solution and of the blank test solution to micrograms of copper per millilitre by means of the calibration graph (8.4).

The copper content w_{Cu}, expressed as a percentage by mass, is given by Formula (1).

$$w_{\mathrm{Cu}} = \frac{(\rho_{\mathrm{Cu},1} - \rho_{\mathrm{Cu},0}) \times D \times 100}{10^6} \times \frac{100}{m}$$

$$= \frac{(\rho_{\mathrm{Cu},1} - \rho_{\mathrm{Cu},0}) \times D}{100m} \quad (1)$$

where

m	is the mass, expressed in grams, of the test portion;
$\rho_{\mathrm{Cu},1}$	is the concentration, expressed in micrograms per millilitre, of copper in the test solution derived from the calibration graph (8.4);
$\rho_{\mathrm{Cu},0}$	is the concentration, expressed in micrograms per millilitre, of copper in the blank test (8.2);
D	is the dilution factor in 8.3.1.2;
$D = 1$	for samples prepared in accordance with 8.3.1.2 a);

$D = 10$ for samples prepared in accordance with 8.3.1.2 b);

$D = 50$ for samples prepared in accordance with 8.3.1.2 c).

10 Precision

A planned trial of this method was carried out by 14 laboratories, at nine levels of copper, each laboratory making three determinations of the copper content at each level.

NOTE 1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725-1, i.e. one operator, same apparatus, identical operating conditions, same calibration, and a minimum period.

NOTE 2 The third determination was carried out at a different time (on a different day) by the same operator as in NOTE 1 using the same apparatus with a new calibration.

The test samples used are listed in Table B.1, and the experimental precision data obtained are shown in Table B.2.

The results obtained were treated statistically in accordance with ISO 5725-2 and ISO 5725-3.

A graphical representation of the experimental precision data is given in Annex C.

The smoothed precision data, expressed as a percentage (mass fraction), shown in Table 4 were calculated from the relationships between the copper content mean values and repeatability limit and reproducibility limits experimental data (see Annex B and Figure C.1).

Table 4 — Precision data (smoothed values)

Copper content % (mass fraction)	**Repeatability limit** % (mass fraction)	**Reproducibility limits** % (mass fraction)	
	r	R_w	R
0,003	0,000 2	0,000 3	0,000 5
0,005	0,000 3	0,000 5	0,000 7
0,01	0,000 5	0,000 8	0,001 3
0,05	0,001 6	0,002 7	0,004 3
0,10	0,003	0,005	0,007
0,20	0,005	0,008	0,012
0,50	0,010	0,015	0,025
1,00	0,017	0,025	0,043
2,00	0,029	0,042	0,073
3,00	0,040	0,057	0,100

11 Test report

The test report shall include at least the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis or of the test report;

b) a reference to this document, i.e. ISO 4943:2022;

c) results and unit in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this document, or any optional operation which might have influenced the results.

Annex A
(normative)

Procedures for the determination of instrumental criteria

A.1 Determination of minimum precision

Nebulize the most concentrated calibration solution 10 times to obtain 10 individual absorbance readings A_{Ai} and calculate the mean value $\bar{A}_A$.

Nebulize the least concentrated calibration solution (excluding the zero member) 10 times to obtain 10 individual absorbance readings A_{Bi} and calculate the mean value $\bar{A}_B$.

The standard deviations s_A and s_B of the most and least concentrated calibration solutions respectively are obtained from Formulae (A.1 and A.2):

$$s_A = \sqrt{\frac{\sum (A_{Ai} - \bar{A}_A)^2}{9}} \quad \text{(A.1)}$$

$$s_B = \sqrt{\frac{\sum (A_{Bi} - \bar{A}_B)^2}{9}} \quad \text{(A.2)}$$

The minimum precisions of the most and least concentrated calibration solutions are obtained from $s_A \times 100 / \bar{A}_A$ and $s_B \times 100 / \bar{A}_A$, respectively.

A.2 Determination of limit of detection, ρ_{LOD}

Prepare two solutions, each containing the same matrix concentration as the sample solution, but with the element of interest at the following known concentration:

— ρ'_{Cu} µg/ml to give an absorbance A' of approximately 0,01;

— matrix blank to give an absorbance A_0.

Nebulize the ρ'_{Cu} solution and blank solution 10 times each and record each reading for about 10 s with sufficient scale expansion to make the fluctuation in signal clearly visible.

Obtain the mean absorbance readings $\bar{A}'$ and $\bar{A}_0$.

The standard deviation $s_{A'}$,is given by Formula (A.3):

$$s_{A'} = \sqrt{\frac{\sum (A'_i - \bar{A}')^2}{9}} \quad \text{(A.3)}$$

where

A'_i is each individual measured absorbance reading;

$\bar{A}'$ is the mean value of A'_i.

The limit of detection, ρ_{LOD}, is given by Formula (A.4):

$$\rho_{\mathrm{LOD}} = \frac{\rho'_{\mathrm{Cu}} \times s_{A'} \times k}{\overline{A'} - \overline{A_0}} \tag{A.4}$$

(k is normally taken as 4,65)

A.3 Criterion for calibration linearity

Having established the calibration graph, before the application of any curve-straightening device, obtain the net absorbance value, A, corresponding to the top 20 % of the concentration range and the net absorbance, B, corresponding to the bottom 20 % of the concentration range (see Figure A.1). Calculate A / B. This shall not be less than 0,7.

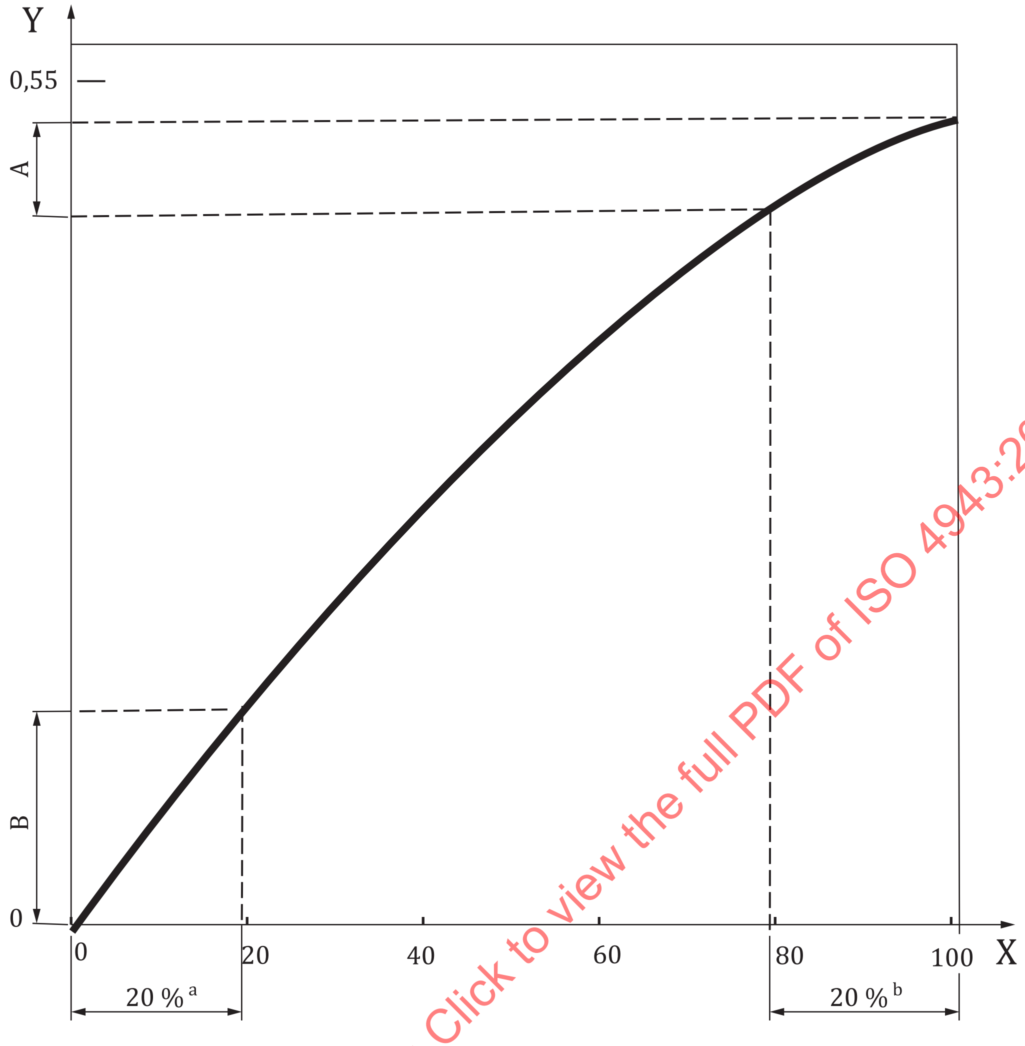
A.4 Determination of characteristic concentration, $\rho_{\mathrm{Cu},k}$

Prepare a solution containing the same matrix concentration as the sample solution, but with the element of interest at the following known concentration:

— ρ_{Cu} µg/ml to give an absorbance, A, of approximately 0,1.

Nebulize the ρ_{Cu} solution and the blank solution without scale expansion and measure the absorbances A and A_0. The characteristic concentration, $\rho_{\mathrm{Cu},k}$, is given by Formula (A.5):

$$\rho_{\mathrm{Cu},k} = \frac{\rho_{\mathrm{Cu}} \times 0{,}004\,4}{A - A_0} \tag{A.5}$$



Key

X concentration scale

Y net absorbance

[a] Bottom 20 % of the concentration range.

[b] Top 20 % of the concentration range.

Figure A.1 — Criterion for calibration linearity