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Steel and cast iron — Determination of copper — 2,2’-Biquinoline spectrophotometric method

Aciers et fontes — Détermination du cuivre — Méthode spectrophotométrique au 2,2’-biquinolyle

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Contents

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Foreword

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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).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

This second edition cancels and replaces the first edition (ISO 4946:1984), which has been technically revised to include the following changes:

- correction of the specification of plotting the calibration graphs in 7.4.3;
- editorial revision of some items in accordance with the updated ISO/IEC Directives, Part 2.

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Steel and cast iron — Determination of copper — 2,2’-Biquinoline spectrophotometric method

1 Scope

This International Standard specifies a spectrophotometric method for the determination of copper in steel and cast iron by 2,2’-biquinoline.

The method is applicable to the determination of copper mass fraction in the range of 0,02 % and 5 %.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 Principle

Dissolution of a test portion in appropriate acids.

Fuming with perchloric acid to remove hydrochloric and nitric acids and dehydrate silicic acid.

Reduction of copper(II) to copper(I) in hydrochloric acid solution by means of ascorbic acid. Formation of a coloured compound of copper(I) with 2,2’-biquinoline.

Spectrophotometric measurement at a wavelength of about 545 nm.

4 Reagents

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

4.1 High-purity iron, containing copper 0,001 % (mass fraction) or less.

4.2 Hydrochloric acid, ρ approximately 1,19 g/ml.

4.3 Nitric acid, ρ approximately 1,40 g/ml.

4.4 Perchloric acid, ρ approximately 1,54 g/ml.

WARNING — Perchloric acid vapour might cause explosions in the presence of ammonia, nitrous fumes or organic material in general.

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Perchloric acid, ρ approximately 1,67 g/ml, may also be used. 100 ml of perchloric acid, ρ approximately 1,54 g/ml is equivalent to 79 ml of perchloric acid, ρ approximately 1,67 g/ml.

4.5 **Perchloric acid**, ρ approximately 1,54 g/ml, diluted 1 + 7.

4.6 **Dimethylformamide (*N*,*N*-dimethylformamide)**, ρ approximately 0,944 g/ml.

WARNING — Dimethylformamide is a hazardous substance and can cause birth defects. It should be handled with safety gloves in a fume hood.

4.7 **Ascorbic acid**, 200 g/l solution.

Dissolve 20 g of ascorbic acid in water, dilute to 100 ml with water and mix.

Prepare this solution immediately before use.

4.8 **2,2’-Biquinoline solution**.

Dissolve 0,60 g of 2,2’-biquinoline (cuproine, 2,2’-diquinolyl) in dimethylformamide (4.6), dilute to 1 l with the same dimethylformamide and mix.

Keep this solution in a dark-coloured glass flask and protect it from the light.

4.9 **Copper standard solution**, 1 g/l.

Weigh, to the nearest 0,001 g, 1,000 g of high purity copper and dissolve in the minimum of nitric acid (4.3).

Heat to boiling to remove nitrous fumes. Cool and transfer the solution quantitatively to 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 copper.

4.10 **Copper standard solution**, 0,05 g/l.

Transfer 25,0 ml of the copper standard solution (4.9) to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,05 mg of copper.

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5 Apparatus

All volumetric glassware shall be Class A, in accordance with ISO 648 and ISO 1042.

Ordinary laboratory apparatus and the following shall be used.

Spectrophotometer, suitable for measuring the absorbance of the solution at a wavelength of 545 nm with cells of 2 cm or 4 cm optical path length.

6 Sampling

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

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7 Procedure

7.1 Test portion

Weigh, to the nearest 0,001 g, approximately 0,5 g of the test sample.

7.2 Blank test

In parallel with the determination and following the same procedure, carry out two blank tests using the same quantities of all the reagents but using, to the nearest 0,001 g, approximately 0,5 g of pure iron (4.1) instead of test portion.

7.3 Determination

7.3.1 Preparation of the test solution

Introduce the test portion (7.1) into a 250 ml beaker. Add 10 ml of hydrochloric acid (4.2) and 5 ml of nitric acid (4.3). Cover the beaker with a watch-glass and heat until acids action ceases.

NOTE For samples of high chromium content, first dissolve in hydrochloric acid (4.2) and then, when all effervescence has ceased, oxidize by adding nitric acid (4.3), drop by drop.

Add 10 ml of perchloric acid (4.4) and evaporate to fuming. Continue fuming for 3 min.

Cool, dissolve the salts with 20 ml of water, transfer the solution quantitatively to a one-mark volumetric flask of suitable capacity (see Table 1), dilute to the mark with water and mix.

Filter by decantation through a dry filter to remove any residue or precipitate, e.g. graphite, silica, tungstic acid. Collect the filtrate in a dry beaker, discarding the first fractions of the filtrate.

7.3.2 Colour development

Take an aliquot portion, according to the expected copper content, as indicated in Table 1.

Table 1 — Volume of test solution and aliquot portion

Copper content % (mass fraction)	Volume of test solution ml	Volume of aliquot portion ml
0,02 to 0,3	100	10
0,3 to 0,6	100	5
0,6 to 1,5	250	5
1,5 to 5,0	500	5

Transfer the selected aliquot portion to a 50 ml one-mark volumetric flask. If the aliquot portion is 5 ml, add 5 ml of perchloric acid (4.5).

Add, in the following order, shaking after each addition:

— 5 ml of ascorbic acid solution (4.7);

— 25 ml of 2,2’-biquinoline solution (4.8).

Dilute to the mark with water and mix. Cool for 5 min in a water-bath at about 20 °C.

Finally, readjust the volume and mix again.

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7.3.3 Preparation of the compensating solution

Transfer an aliquot portion of the test solution (7.3.1) similar to the aliquot portion for the development of the colour (7.3.2) to a 50 ml one-mark volumetric flask. If the aliquot portion is 5 ml, add 5 ml of perchloric acid (4.5).

Add, in the following order, shaking after each addition:

- 5 ml of ascorbic acid solution (4.7);
- 25 ml of dimethylformamide solution (4.6).

Dilute to the mark with water and mix. Cool for 5 min in a water-bath at about 20 °C.

Finally, readjust the volume and mix again.

7.3.4 Spectrophotometric measurement

Carry out the spectrophotometric measurement of the test solution (7.3.1) at a wavelength of about 545 nm, in a cell of 2 cm optical path length, after adjusting the spectrophotometer (Clause 5) to zero absorbance in relation to the compensating solution (7.3.3).

For copper contents below 0,06 % (mass fraction), 4 cm cells may be used if the sensitivity of the spectrophotometer is not sufficient with 2 cm cells.

7.4 Establishment of the calibration graph

7.4.1 Preparation of the calibration solutions

Into each of a series of 100 ml beakers, add 0,5 g ± 0,01 g of high purity iron (4.1) and 10 ml of hydrochloric acid (4.2). Cover with a watch-glass and heat gently until dissolved, then oxidize by adding nitric acid (4.3) drop by drop. Add the following volumes of the standard copper solution (4.10) to the beakers, respectively: 0 ml, 2 ml, 5 ml, 10 ml, 20 ml, 30 ml, 40 ml and 50 ml.

Add 10 ml of perchloric acid (4.4) and evaporate to fumes. Continue fuming for 3 min.

Cool, dissolve the salts with 20 ml of water; transfer the solutions quantitatively to 100 ml one-mark volumetric flasks, dilute to the mark with water and mix.

From each volumetric flask, take 10,0 ml of the solution and transfer respectively into a series of 50 ml one-mark volumetric flasks. The zero term represents the compensating solution.

For the colour development, proceed as directed in 7.3.2, beginning at “Add, in the following order...”.

The copper concentrations in the 50 ml calibration solutions are respectively 0 µg, 0,2 µg, 0,5 µg, 1 µg, 2 µg, 3 µg, 4 µg and 5 µg of copper per millilitre.

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7.4.2 Spectrophotometric measurement

Carry out the spectrophotometric measurement of absorbance of each calibration solution (7.4.1) at a wavelength of about 545 nm, in a cell of 2 cm optical path length, using the zero term calibration solution as the compensating solution as described in 7.3.4.

7.4.3 Calibration graph

Establish the calibration graph by plotting the net absorbance values against the copper concentrations, expressed in micrograms per millilitre, in the calibration solutions.

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8 Expression of results

Convert the absorbance (7.3.4) into the corresponding concentration, expressed in micrograms of copper per millilitre, in the colour-developed test solution by using the calibration graph (7.4.3).

The copper content (C_{Cu}), expressed as a mass fraction (%), is given by Formula (1), Formula (2) and Formula(3):

$$C_{\mathrm{Cu}} = \left(\rho_{\mathrm{Cu1}} - \rho_{\mathrm{Cu0}}\right) \times \frac{1}{10^6} \times \frac{V_0}{V_1} \times \frac{V_{\mathrm{t}}}{m} \times 100 \tag{1}$$

$$C_{\mathrm{Cu}} = \left(\rho_{\mathrm{Cu1}} - \rho_{\mathrm{Cu0}}\right) \times \frac{1}{10^6} \times \frac{V_0}{V_1} \times \frac{50}{m} \times 100 \tag{2}$$

$$C_{\mathrm{Cu}} = \left(\rho_{\mathrm{Cu1}} - \rho_{\mathrm{Cu0}}\right) \times \frac{5V_0}{10^3 V_1 m} \tag{3}$$

where

m	is the mass of the test portion (7.1), in grams;
V_0	is the volume of the test solution (see Table 1), in millilitres;
V_1	is the volume of the aliquot portion (see Table 1), in millilitres;
V_{t}	is the volume of the colour-developed test solution (7.3.2), in millilitres;
ρ_{Cu0}	is the concentration, of copper in the blank test solution (corrected for its compensating solution), expressed in micrograms per millilitre;
ρ_{Cu1}	is the concentration of copper in the test solution (corrected for its compensating solution), expressed in micrograms per millilitre.

9 Precision

9.1 General

A planned trial of this method was carried out by six laboratories, at five levels of copper, each laboratory making three to five determinations at each level.

The results obtained were treated statistically in accordance with ISO 5725:1986[1].

The data obtained showed a logarithmic relationship between copper content and repeatability or reproducibility of the test results, as summarized in Table 2. The graphic presentation of the data is given in Annex B.

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Table 2 — Repeatability and reproducibility limits

Copper content level % (mass fraction)	Repeatability limit *r*	Reproducibility limit *R*
0,02	0,000 5	0,003 2
0,05	0,001 3	0,006 0
0,10	0,002 4	0,009 6
0,20	0,004 6	0,015
0,50	0,011	0,029
1,00	0,021	0,046
2,00	0,040	0,073
5,00	0,093	0,137

9.2 Repeatability

The difference between two single and independent results found on identical test material by one analyst using the same apparatus within a short time interval in the normal and correct operation of the test method will exceed the repeatability, *r*, only in one case in 20 cases.

9.3 Reproducibility

The difference between two single and independent results found by two operators working in different laboratories on identical test material in the normal and correct operation of the test method will exceed the reproducibility, *R*, only in one case in 20 cases.

10 Test report

The test report shall include 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) method used with reference to this International Standard, i.e. ISO 4946;

c) results and unit in which they are expressed;

d) any unusual features noted during the determination;

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

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Annex A
(informative)

Additional information on the international interlaboratory test

Data given in Table 2 has been derived from the results of the international trial carried out in 1978 on four steel samples and two cast iron samples in three countries involving six laboratories.

The results of the trial were reported in document 17/1 N 432, September 1980.

The test samples used are given in Table A.1.

Table A.1 — Test samples

Sample		Copper content % (mass fraction)	
		Certified	**Found**
BCS 434	(Plain carbon steel)	0,017	0,016 9
BCS 407	(Low alloy steel)	0,43	0,434
BCS 172/3	(Alloy cast iron)	1,50	1,521
BCS 365	(Alcomax III)	2,70	2,719
BCS 173/1	(Austenitic cast iron)	5,05	5,105

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