
International Standard 4946

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Steel and cast iron — Determination of copper content — 2,2'-Diquinolyl spectrophotometric method

Aciers et fontes — Dosage du cuivre — Méthode spectrophotométrique au 2,2'-biquinolyle

First edition — 1984-12-15

Corrected and reprinted 1986-12-15

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UDC 669.13/.14 : 543.42 : 546.56

Ref. No. ISO 4946-1984 (E)

Descriptors: steels, cast iron, chemical analysis, determination of content, copper, spectrophotometric analysis.

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 4946 was prepared by Technical Committee ISO/TC 17, *Steel*.

Steel and cast iron — Determination of copper content — 2,2'-Diquinolyl spectrophotometric method

1 Scope and field of application

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

The method is applicable to copper contents between 0,02 and 5 % (m/m).

2 Reference

ISO/R 377, *Selection and preparation of samples and test pieces for wrought steel*.

3 Principle

Dissolution of a test portion with 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'-diquinolyl.

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 distilled water or water of equivalent purity, free from copper.

4.1 High-purity iron, containing 0,001 % (m/m) or less of copper.

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.

NOTE — 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.

4.7 Ascorbic acid, 200 g/l solution.

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

Prepare this solution immediately before use.

4.8 2,2'-Diquinolyl, solution.

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

Keep this solution in a dark-coloured glass receptacle and protected from the light.

4.9 Copper, standard solutions.

4.9.1 Copper, standard solution, corresponding to 1,0 g of Cu per litre.

Weigh, to the nearest 0,000 1 g, 1,000 0 g of high purity copper and dissolve in a minimum of the 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 and mix.

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

4.9.2 Copper, standard solution, corresponding to 0,050 g of Cu per litre.

Transfer 50,0 ml of the copper standard solution (4.9.1) to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

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

5 Apparatus

Ordinary laboratory apparatus and

5.1 Spectrophotometer.

6 Sampling

Carry out sampling in accordance with ISO/R 377 or appropriate national standards for cast iron.

7 Procedure

WARNING

a) **Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic material in general.**

b) **Dimethylformamide is a hazardous substance and should not be handled by pregnant women. It should be handled with safety gloves in a fume hood.**

7.1 Test portion

Weigh, to the nearest 0,001 g, approximately 0,5 g (*m*) of the test sample.

7.2 Blank test

Parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all the reagents.

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 the hydrochloric acid (4.2) and 5 ml of the nitric acid (4.3), cover the beaker with a watch-glass and heat until solvent action ceases.

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

Add 10 ml of the 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 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

Copper content	Volume of test solution (7.3.1)	Volume of aliquot portion
% (<i>m/m</i>)	ml	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 the perchloric acid (4.5).

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

- 5 ml of the ascorbic acid solution (4.7) ;
- 25 ml of the 2,2'-diquinolyl solution (4.8).

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

Finally, readjust to volume and mix again.

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

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

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

Finally, readjust to volume and mix again.

7.3.4 Spectrophotometric measurement

Carry out the spectrophotometric measurement of the test solution at a wavelength of about 545 nm, in a cell of 2 cm optical path length, after having adjusted the spectrophotometer (5.1) to zero absorbance in relation to the compensating solution (7.3.3).

NOTE — For copper contents below 0,06 % (*m/m*), 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 calibration solutions

To each of seven 100 ml beakers, add $0,5 \pm 0,01$ g of the high purity iron (4.1) and 10 ml of the hydrochloric acid (4.2). Cover with a watch-glass and warm gently until dissolved, then oxidize by adding the nitric acid (4.3) drop by drop. By means of pipettes, add respectively to the beakers the following quantities of the standard copper solution (4.9.2) : 0 ; 5 ; 10 ; 20 ; 30 ; 40 ; and 50 ml.

Add 10 ml of the perchloric acid (4.4) and evaporate to fuming. 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 and mix.

From each volumetric flask take 10,0 ml of the solution and transfer respectively to 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 0,5; 1; 2; 3; 4; and 5 µg of Cu per millilitre.

7.4.2 Spectrophotometric measurement

Carry out the spectrophotometric measurement of absorbance of each calibration solution (7.4.1) using the calibration solution with 0 ml of the standard copper solution as the compensating solution in accordance with the directions given in 7.3.4.

7.4.3 Plotting of the calibration graph and calculation of the angular coefficient a

Prepare the calibration graph by plotting the net absorbance values, converted to measurement in a 1 cm optical path length cell, against the copper concentrations, expressed in micrograms per millilitre, in the measured solutions. Calculate the angular coefficient a from the slope of the calibration graph, if it is a straight line.

8 Expression of results

8.1 When the calibration graph is not a straight line

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

The copper (Cu) content, expressed as a percentage by mass, is given by the formula

$$\begin{aligned} & (\varrho_{\text{Cu}1} - \varrho_{\text{Cu}0}) \times \frac{1}{10^6} \times \frac{1}{b} \times \frac{V_0}{V_1} \times \frac{V_t}{m} \times 100 \\ &= (\varrho_{\text{Cu}1} - \varrho_{\text{Cu}0}) \times \frac{1}{10^6} \times \frac{1}{b} \times \frac{V_0}{V_1} \times \frac{50}{m} \times 100 \\ &= (\varrho_{\text{Cu}1} - \varrho_{\text{Cu}0}) \frac{5V_0}{10^3 b V_1 m} \end{aligned}$$

where

b is the optical path length, in centimetres, of the cell used for the measurements;

m is the mass, in grams, of the test portion (7.1);

V_0 is the volume, in millilitres, of the test solution (7.3.1);

V_1 is the volume, in millilitres, of the aliquot portion (table 1);

V_t is the volume, in millilitres, of the colour-developed test solution (7.3.2);

$\varrho_{\text{Cu}0}$ is the concentration, expressed in micrograms per millilitre, of copper in the blank test solution (corrected for its compensating solution);

$\varrho_{\text{Cu}1}$ is the concentration, expressed in micrograms per millilitre, of copper in the test solution (corrected for its compensating solution).

8.2 When the calibration graph is a straight line

The copper (Cu) content, expressed as a percentage by mass, is given by the formula

$$\begin{aligned} & \frac{A_1 - A_0}{a} \times \frac{1}{10^6} \times \frac{1}{b} \times \frac{V_0}{V_1} \times \frac{V_t}{m} \times 100 \\ &= \frac{A_1 - A_0}{a} \times \frac{1}{10^6} \times \frac{1}{b} \times \frac{V_0}{V_1} \times \frac{50}{m} \times 100 \\ &= \left(\frac{A_1 - A_0}{a} \right) \frac{5V_0}{10^3 b V_1 m} \end{aligned}$$

where

a is the angular coefficient or the absorbance per microgram of Cu per millilitre of solution measured with an optical path length of 1 cm;

A_0 is the absorbance of the blank test solution measured in relation to its compensating solution (7.2);

A_1 is the absorbance of the test solution measured in relation to its compensating solution (7.3.3);

b is the optical path length, in centimetres, of the cell used for the measurements;

m is the mass, in grams, of the test portion (7.1);

V_0 is the volume, in millilitres, of the test solution (7.3.1);

V_1 is the volume, in millilitres, of the aliquot portion (table 1);

V_t is the volume, in millilitres, of the colour-developed test solution (7.3.2).

9 Precision

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, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests*.

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 figures is given in annex B.

Table 2

Level copper % (m/m)	<i>r</i>	<i>R</i>
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

The difference between two independent single results found on identical test material by one analyst using the same apparatus within a short time interval will exceed the repeatability *r*, on average not more than once in 20 cases, in the normal and correct operation of the method.

The difference between two single and independent results found by two operators working in different laboratories on identical test material will exceed the reproducibility *R*, on average not more than once in 20 cases in the normal and correct operation of the method.

10 Test report

The test report shall include the following information:

- the method used by reference to this International Standard;
- the results, and the form in which they are expressed;
- any unusual features noted during the determination;
- any operation not specified in this International Standard, or any optional operation which may have influenced the result.