INTERNATIONAL STANDARD 1053

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Zinc — Determination of copper content — Spectrophotometric method

Zinc — Dosage du cuivre — Méthode spectrophotométrique

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is caried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up 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.

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.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 18 has reviewed ISO Recommendation R 1053 and found it technically suitable for transformation. International Standard ISO 1053 therefore replaces ISO Recommendation R 1053-1969 to which it is technically identical.

ISO Recommendation R 1053 was approved by the Member Bodies of the following countries :

Australia	Greece	Poland
Belgium	India	South Africa, Rep. of
Brazil	Iran	Spain
Canada	Israel	Sweden
Chile	Italy	Turkey
Czechoslovakia	Korea, Dem. P. Rep. of	United Kingdom
Egypt, Arab Rep. of	Korea, Rep. of	U.S.A.
France	New Zealand	Yugoslavia
Germany	Norway	

No Member Body expressed disapproval of the Recommendation.

No Member Body disapproved the transformation of ISO/R 1053 into an International Standard.

Printed in Switzerland

Zinc — Determination of copper content — Spectrophotometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies two spectrophotometric methods for the determination of the copper content of zinc.

The methods are applicable to all types of zinc defined in ISO/R 752.

The first method permits the determination of copper contents between 0,000 5 and 0,005 %.

The second method permits the determination of copper contents between 0,002 5 and 0,1 %.

2 REFERENCES

ISO/R 752, *Zinc ingots.*

ISO 3751, *Zinc ingots — Selection and preparation of samples for chemical analysis.* [1]

3 FIRST SPECTROPHOTOMETRIC METHOD

(Copper contents between 0,000 5 and 0,005 %)

3.1 Principle

Spectrophotometric determination of the violet colour obtained with copper in the presence of oxalyldihydrazide and acetaldehyde between pH 9,0 and 10,0.

3.2 Reagents

During the analysis, use only reagents of analytical reagent grade and distilled or demineralized water, free from copper.

3.2.1 Hydrochloric acid, ρ 1,19 g/ml.

3.2.2 Hydrogen peroxide, 30 % H_2O_2 (*m/m*).

3.2.3 Citric acid monohydrate, 500 g/l solution.

3.2.4 Ammonia solution, ρ 0,91 g/ml.

3.2.5 Acetaldehyde, 40 % (*V/V*) methanolic solution.[2]

As the boiling point of acetaldehyde is 21 °C and heat is produced when acetaldehyde and methanol are mixed, it is advisable to cool, with cold water, the vessel in which the reagents are mixed.

3.2.6 Oxalyldihydrazide, 2,5 g/l aqueous solution.

Heat gently to dissolve.

3.2.7 Acetaldehyde-oxalyldihydrazide mixture.

Mix 1 volume of acetaldehyde solution (3.2.5) and 1 volume of oxalyldihydrazide solution (3.2.6). Allow to stand for 2 h. Filter if necessary.

3.2.8 Copper standard solution, 25 mg/l.

Dissolve at room temperature 0,500 g of electrolytic copper, weighed to the nearest 0,001 g, in 20 ml of hydrochloric acid (3.2.1) and 5 ml of hydrogen peroxide (3.2.2). After dissolution, decompose the excess of hydrogen peroxide by boiling. Cool. Transfer quantitatively to a 1 l volumetric flask. Dilute to the mark and mix. Transfer 50 ml of this solution to a 1 l volumetric flask. Dilute to the mark and mix.

1 ml of this solution contains 0,025 mg of copper.

3.2.9 Zinc solution, free from copper.

Transfer 200 g of pure zinc to a 2 l beaker and dissolve with about 750 ml of hydrochloric acid (3.2.1). After dissolution, evaporate to a syrupy consistency, then allow to cool. Dilute to about 400 ml. Add 20 g of zinc powder and stir for about 45 min (with a magnetic agitator). Filter through a fine filter into a 500 ml volumetric flask. Dilute to the mark and mix.

25 ml of this solution contain 10 g of zinc.

3.2.10 Nickel chloride solution.

Dissolve 0,5 g of pure nickel in the minimum amount of hydrochloric acid (3.2.1). Make up the volume to 1 l.

1) At present at the stage of draft.

2) This alcoholic solution has the great advantage of being more stable than the aqueous solution.

3.3 Apparatus

Ordinary laboratory apparatus and

3.3.1 Spectrophotometer, wavelength 540 nm, and **1 cm cells.**

3.4 Sampling

Sampling shall be carried out in accordance with the requirements of ISO 3751.

3.5 Procedure

3.5.1 *Test portion*

Weigh, to the nearest 0,01 g, 10 g of the test sample.

3.5.2 *Blank test*

Simultaneously with the actual determination, carry out a blank test proceeding as follows :

3.5.2.1 PREPARATION OF THE SOLUTION

3.5.2.1.1 Transfer 25 ml of the zinc solution free from copper (3.2.9) to a 250 ml beaker.

3.5.2.1.2 Add 50 ml of hydrochloric acid (3.2.1).

3.5.2.1.3 Add a few drops of hydrogen peroxide (3.2.2).

3.5.2.1.4 Continue the procedure as outlined in 3.5.4.1.3 to 3.5.4.1.5.

3.5.2.2 DEVELOPMENT OF THE COLOUR

Continue the procedure for the development of the colour as outlined in 3.5.4.2.

3.5.2.3 SPECTROPHOTOMETRIC MEASUREMENT

Measure the absorbance of the solution with the spectrophotometer (3.3.1) as outlined in 3.5.4.3.

3.5.3 *Plotting of the calibration curve*

3.5.3.1 Into a series of 250 ml volumetric flasks, introduce 0, 4, 8, 12, 16 and 20 ml respectively of the standard copper solution (3.2.8), corresponding to 0 — 0,1 — 0,2 — 0,3 — 0,4 and 0,5 mg of copper.

3.5.3.2 Add 25 ml of the zinc solution free from copper (3.2.9).

3.5.3.3 Evaporate to a syrupy consistency and continue the procedure as outlined in 3.5.4.1.4 to 3.5.4.2.2 inclusive.

3.5.3.4 Measure the absorbance of the solution against the solution to which no copper has been added.

3.5.4 *Determination*

3.5.4.1 PREPARATION OF THE SOLUTION

3.5.4.1.1 Transfer the test portion to a 250 ml beaker and attack with 50 ml of hydrochloric acid (3.2.1).[1)]

3.5.4.1.2 Oxidize and complete the solution by adding a few drops of hydrogen peroxide (3.2.2).

3.5.4.1.3 Evaporate to a syrupy consistency.

3.5.4.1.4 Allow to cool. Take up with water. Heat gently to redissolve any residue. Cool. Transfer quantitatively to a 50 ml volumetric flask. Dilute to the mark and mix.

3.5.4.1.5 Transfer a 10 ml aliquot to a 50 ml volumetric flask.

Add successively

- 2 ml of citric acid solution (3.2.3);
- 15 ml of ammonia solution (3.2.4).

Cool.

3.5.4.2 DEVELOPMENT OF THE COLOUR

3.5.4.2.1 Add 20 ml of the acetaldehyde-oxalyldihydrazide mixture (3.2.7). Mix. Allow to cool. Dilute to the mark and mix.

3.5.4.2.2 Allow at least 60 min for the colour to develop.

3.5.4.3 SPECTROPHOTOMETRIC MEASUREMENT

Measure the absorbance of the solution against the blank solution at a wavelength of 540 nm in the spectrophotometer (3.3.1).

3.6 Expression of results

Determine the copper content by means of the calibration curve (see 3.5.3).

3.7 Test report

The test report shall mention the method used and the results obtained. It shall also mention all operational details not provided for in this International Standard, or any optional details, as well as any circumstances which could have influenced the results.

The test report shall include all details required for complete identification of the sample.

1) If dissolution is very difficult, 2 ml of nickel chloride solution (3.2.10) may be added to expedite the attack.

4 SECOND SPECTROPHOTOMETRIC METHOD

(Copper contents between 0,002 5 and 0,1 %.)

4.1 Principle

Spectrophotometric determination of the violet colour obtained with copper in the presence of oxalyldihydrazide and acetaldehyde between pH 9,0 and 10,0.

4.2 Reagents

During the analysis, use only reagents of analytical reagent grade and distilled or demineralized water, free from copper.

4.2.1 Hydrochloric acid, ρ 1,19 g/ml.

4.2.2 Hydrogen peroxide, 30 % H_2O_2 (*m/m*).

4.2.3 Citric acid monohydrate, 500 g/l solution.

4.2.4 Ammonia solution, ρ 0,91 g/ml.

4.2.5 Acetaldehyde, 40 % (*V/V*) methanolic solution.[1)]

As the boiling point of acetaldehyde is 21 °C and heat is produced when acetaldehyde and methanol are mixed, it is advisable to cool, with cold water, the vessel in which the reagents are mixed.

4.2.6 Oxalyldihydrazide, 2,5 g/l aqueous solution.

Heat gently to dissolve.

4.2.7 Acetaldehyde-oxalyldihydrazide mixture.

Mix 1 volume of acetaldehyde solution (4.2.5) and 1 volume of oxalyldihydrazide solution (4.2.6). Allow to stand for 2 h. Filter if necessary.

4.2.8 Copper standard solution, 10 mg/l.

Dissolve at room temperature 0,200 g of electrolytic copper, weighed to the nearest 0,000 5 g, in 5 ml of hydrochloric acid (4.2.1) and 2 ml of hydrogen peroxide (4.2.2). After dissolution, decompose the excess of hydrogen peroxide by boiling. Cool. Transfer quantitatively to a 1 l volumetric flask. Dilute to the mark and mix. Transfer 50 ml of this solution to a 1 l volumetric flask. Dilute to the mark and mix.

1 ml of this solution contains 0,01 mg of copper.

4.2.9 Nickel chloride solution.

Dissolve 0,5 g of pure nickel in the minimum amount of hydrochloric acid (4.2.1). Make up the volume to 1 l.

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Spectrophotometer, wavelength 540 nm, and **1 cm cells.**

4.4 Sampling

Sampling shall be carried out in accordance with the requirements of ISO 3751.

4.5 Procedure

4.5.1 *Test portion*

Weigh, to the nearest 0,01 g, 10 g of the test sample.

4.5.2 *Blank test*

Simultaneously with the actual determination, carry out a blank test proceeding as follows :

4.5.2.1 PREPARATION OF THE SOLUTION

4.5.2.1.1 Evaporate 50 ml of ammonia solution (4.2.4) to dryness in a 250 ml beaker.

4.5.2.1.2 Add 50 ml of hydrochloric acid (4.2.1) and evaporate to a final volume of 1 to 2 ml. Cool.

4.5.2.1.3 Take up with water and transfer quantitatively to a volumetric flask (see 4.5.4.1.4). Dilute to the mark and mix.

4.5.2.1.4 Transfer a 10 ml aliquot to a 50 ml volumetric flask.

Add successively

- 2 ml of citric acid solution (4.2.3);
- 5 ml of ammonia solution (4.2.4).

Cool.

4.5.2.2 DEVELOPMENT OF THE COLOUR

4.5.2.2.1 Add 20 ml of the acetaldehyde-oxalyldihydrazide mixture (4.2.7). Mix. Allow to cool. Make up the volume to 50 ml with water. Mix.

4.5.2.2.2 Allow at least 60 min for the colour to develop.

4.5.2.3 SPECTROPHOTOMETRIC MEASUREMENT

Measure the absorbance of the solution as indicated in 4.5.4.3.

1) This alcoholic solution has the great advantage of being more stable than the aqueous solution.

4.5.3 *Plotting of the calibration curve*

4.5.3.1 Into a series of 50 ml volumetric flasks, introduce 0, 2, 4, 6, 8 and 10 ml respectively of the standard copper solution (4.2.8), corresponding to 0 — 0,02 — 0,04 — 0,06 — 0,08 and 0,1 mg of copper.

4.5.3.2 Make up to a volume of approximately 10 ml with water.

Add successively

— 2 ml of citric acid solution (4.2.3);

— 5 ml of ammonia solution (4.2.4).

Continue the procedure as outlined in 4.5.4.2.

4.5.3.3 Measure the absorbance of the solution against the solution to which no copper has been added.

4.5.4 *Determination*

4.5.4.1 PREPARATION OF THE SOLUTION

4.5.4.1.1 Transfer the test portion to a 250 ml beaker and attack with 50 ml of hydrochloric acid (4.2.1).[1)]

4.5.4.1.2 Oxidize and complete the solution by adding a few drops of hydrogen peroxide (4.2.2).

4.5.4.1.3 Evaporate to a syrupy consistency.

4.5.4.1.4 Allow to cool. Take up with water. Heat gently to redissolve any residue. Cool. Transfer quantitatively to a volumetric flask as indicated below :

Presumed copper content	Volume of volumetric flask
%	ml
from 0,002 5 to 0,025	250
from 0,01 to 0,1	1 000

Dilute to the mark and mix.

4.5.4.1.5 Transfer a 10 ml aliquot to a 50 ml volumetric flask.

Add successively

— 2 ml of citric acid solution (4.2.3);

— the volume of ammonia solution (4.2.4) given in the following table, according to the dilution chosen under 4.5.4.1.4.

Volume of volumetric flask (see 4.5.4.1.4)	Volume of ammonia solution (4.2.4)
ml	ml
250	7
1 000	5,5

Cool.

4.5.4.2 DEVELOPMENT OF THE COLOUR

4.5.4.2.1 Add 20 ml of the acetaldehyde-oxalyldihydrazide mixture (4.2.7). Mix. Allow to cool. Dilute to the mark and mix.

4.5.4.2.2 Allow at least 60 min for the colour to develop.

4.5.4.3 SPECTROPHOTOMETRIC MEASUREMENT

Measure the absorbance of the solution against the blank solution at a wavelength of 540 nm in the spectrophotometer (4.3.1).

4.6 Expression of results

Determine the copper content by means of the calibration curve (see 4.5.3).

4.7 Test report

The test report shall mention the method used and the results obtained. It shall also mention all operational details not provided for in this International Standard, or any optional details, as well as any circumstances which could have influenced the results.

The test report shall include all details required for complete identification of the sample.

1) If dissolution is very difficult, 2 ml of nickel chloride solution (4.2.9) may be added to expedite the attack.