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R 1053

CHEMICAL ANALYSIS OF ZINC

SPECTROPHOTOMETRIC DETERMINATION OF COPPER

1st EDITION
April 1969

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BRIEF HISTORY

The ISO Recommendation R 1053, *Chemical analysis of zinc – Spectrophotometric determination of copper,* was drawn up by Technical Committee ISO/TC 18, *Zinc and zinc alloys,* the Secretariat of which is held by the Institut Belge de Normalisation (IBN).

Work on this question led, in 1966, to the adoption of a Draft ISO Recommendation.

In November 1967, this Draft ISO Recommendation (No. 1286) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

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

No Member Body opposed the approval of the Draft.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in April 1969, to accept it as an ISO RECOMMENDATION.

ISO Recommendation | R 1053 | April 1969

CHEMICAL ANALYSIS OF ZINC

SPECTROPHOTOMETRIC DETERMINATION OF COPPER

1. SCOPE

This ISO Recommendation describes two spectrophotometric methods for the determination of copper in zinc.

2. FIELD OF APPLICATION

The methods apply to all types of zinc defined in ISO Recommendation R 752, *Zinc ingots*.

The first method permits the determination of copper contents between 0.0005 and 0.005 %.

The second method permits the determination of copper contents between 0.0025 and 0.1 %.

3. FIRST SPECTROPHOTOMETRIC METHOD

(Copper contents between 0.0005 and 0.005 %)

3.1 Principle of the method

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

All the reagents should be of the analytical reagent grade.

Distilled or demineralized water, free from copper, should be used for preparing the solutions and during the actual determination.

3.2.1 *Hydrochloric acid*, $d = 1.19$.

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

3.2.3 *Citric acid monohydrate solution*, 500 g per litre.

3.2.4 *Ammonia solution*, $d = 0.91$.

3.2.5 *Acetaldehyde solution*, 40 % (v/v) in methanol.*

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.

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

3.2.6 *Aqueous solution of oxalyldihydrazide,* 2.5 g per litre.

Heat slightly to dissolve.

3.2.7 *Acetaldehyde-oxalyldihydrazide mixture*

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

3.2.8 *Standard copper solution,* 25 mg per litre.

Dissolve at room temperature 0.500 g of electrolytic copper, weighed to ± 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 litre volumetric flask. Make up to volume with water. Mix. Transfer 50 ml of this solution to a 1 litre volumetric flask. Make up to volume with water. 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 litre 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 3/4 hour (with a magnetic agitator). Filter through a fine filter into a 500 ml volumetric flask. Make up to volume with water. 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 litre.

3.3 Apparatus

3.3.1 *Ordinary laboratory equipment.*

3.3.2 *Spectrophotometer* (wavelength 540 nm and 1 cm cells).

3.4 Sampling

The requirements of ISO Recommendation R . . .,* *Sampling and preparation of samples for analysis,* should apply.

3.5 Procedure

3.5.1 *Test portion.* Weigh a 10 g test portion to ± 0.01 g.

3.5.2 *Blank test.* Simultaneously with the actual determination, carry out a blank test using the same reagents and 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 clauses 3.5.4.1.3 to 3.5.4.1.5.

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* To be prepared later.

3.5.2.2 DEVELOPMENT OF THE COLOUR

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

3.5.2.3 SPECTROPHOTOMETRIC MEASUREMENT

Measure the optical density of the solution with the spectrophotometer as outlined in clause 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 clauses 3.5.4.1.4 to 3.5.4.2.2 inclusive.

3.5.3.4 Measure the optical density 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)*.

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. Make up to volume with water. 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. Make up the volume to 50 ml with water. Mix.

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

3.5.4.3 SPECTROPHOTOMETRIC MEASUREMENT

Measure the optical density of the solution against the blank solution at a wavelength of 540 nm (3.3.2).

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

3.6 Expression of results

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

3.7 Test report

The test report should mention the method used and the results obtained.

It should also mention all operational details not provided for in this ISO Recommendation, or any optional details, as well as any circumstances which could have influence on the results.

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

4. SECOND SPECTROPHOTOMETRIC METHOD

(Copper contents between 0.0025 and 0.1 %)

4.1 Principle of the method

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

All the reagents should be of the analytical reagent grade.

Distilled or demineralized water, free from copper, should be used for preparing the solutions and during the actual determination.

4.2.1 *Hydrochloric acid*, $d = 1.19$.

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

4.2.3 *Citric acid monohydrate solution*, 500 g per litre.

4.2.4 *Ammonia solution*, $d = 0.91$.

4.2.5 *Acetaldehyde solution*, 40 % (v/v) in methanol.*

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 *Aqueous solution of oxalyldihydrazide*, 2.5 g per litre.

Heat gently to dissolve.

4.2.7 *Acetaldehyde-oxalyldihydrazide mixture*

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

4.2.8 *Standard copper solution*, 10 mg per litre.

Dissolve at room temperature 200 mg of electrolytic copper, weighed to ± 0.0005 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 litre volumetric flask. Make up to volume with water. Mix. Transfer 50 ml of this solution to a 1 litre volumetric flask. Make up to volume with water. 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 litre.

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

4.3 Apparatus

4.3.1 *Ordinary laboratory equipment.*

4.3.2 *Spectrophotometer* (wavelength 540 nm and 1 cm cells).

4.4 Sampling

The requirements of ISO Recommendation R . . .,* *Sampling and preparation of samples for analysis,* should apply.

4.5 Procedure

4.5.1 *Test portion.* Weigh a 10 g test portion to ± 0.01 g.

4.5.2 *Blank test.* Simultaneously with the actual determination, carry out a blank test using the same reagents and 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 clause 4.5.4.1.4). Make up to volume with water. 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 minutes for the colour to develop.

4.5.2.3 SPECTROPHOTOMETRIC MEASUREMENT

Measure the optical density of the solution as indicated in clause 4.5.4.3.

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).

and continue the procedure as outlined in clause 4.5.4.2.

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

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* To be prepared later