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Magnesium and its alloys — Determination of nickel — Photometric method using dimethylglyoxime

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FOREWORD

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Magnesium and its alloys — Determination of nickel — Photometric method using dimethylglyoxime

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a photometric method using dimethylglyoxime (oxidized complex) for the determination of nickel in magnesium and its alloys.

The method applies to the determination of nickel contents between 0,000 5 and 0,05 %.

2 PRINCIPLE

Dissolution of a test portion by hydrochloric acid and nitric acid. Complexing of interfering elements by the addition of hydroxylammonium chloride, citric acid and thiourea. Formation of the nickel-dimethylglyoxime complex and extraction of this complex by chloroform.

Passage of the nickel of the nickel-dimethylglyoxime complex into aqueous solution by treatment with dilute hydrochloric acid. Oxidation of the nickel with bromine water and development of the colour by the addition of dimethylglyoxime in ammoniacal medium. Photometric measurement of the coloured complex at the maximum of the absorption curve (wavelength about 445 nm).

3 REAGENTS

During the analysis use only distilled water or water of equivalent purity.

3.1 Hydrochloric acid, ρ approximately 1,18 g/ml, 36 % (*m/m*) solution or approximately 12 N.

3.2 Nitric acid, ρ approximately 1,40 g/ml, 68 % (*m/m*) solution or approximately 15 N.

3.3 Hydroxylammonium chloride, 100 g/l solution.

Dissolve 10 g of hydroxylammonium chloride ($NH_2OH.HCl$) in about 40 ml of water, make up the volume to 100 ml and mix.

Renew this solution each week.

3.4 Citric acid, 300 g/l solution.

Dissolve 300 g of citric acid ($C_6H_8O_7.H_2O$) in water, make up the volume to 1 000 ml and mix.

3.5 Thiourea, 100 g/l solution.

Dissolve 100 g of thiourea (NH_2CSNH_2) in water, make up the volume to 1 000 ml and mix.

3.6 Ammonia, ρ approximately 0,91 g/ml, 25 % (*m/m*) solution or approximately 15 N.

3.7 Dimethylglyoxime, 10 g/l solution in ethanol.

Dissolve 10 g of dimethylglyoxime ($C_4H_8O_2N_2$) in 95 % (*V/V*) ethanol, make up the volume to 1 000 ml with the same ethanol and mix.

3.8 Chloroform ($CHCl_3$), ρ approximately 1,48 g/ml.

3.9 Ammonia, approximately 0,50 % (*m/m*) solution.

Dilute 20 ml of ammonia solution (3.6) with water, make up the volume to 1 000 ml and mix.

3.10 Hydrochloric acid, approximately 1,8 % (*m/m*) solution.

Dilute 50 ml of hydrochloric acid (3.1) with water; make up the volume to 1 000 ml and mix.

3.11 Bromine water, saturated solution at ambient temperature.

The solution should be prepared 24 h before use.

3.12 Nickel, 1 g/l standard solution.

Prepare this solution according to one of the following methods :

3.12.1 Weigh, to the nearest 0,001 g, 1 g of pure nickel (titre 99,7 % or more) and transfer to a tall-form beaker of suitable capacity (600 ml, for example).

Cover with a watch glass, and add 10 ml of water and 10 ml of nitric acid solution (3.2).

Allow the nickel to react slowly, heating gently, if necessary, to complete the attack. Once the reaction is finished, add 10 ml of hydrochloric acid (3.1) and evaporate, carefully, to dryness (do not calcine).

Repeat the treatment with hydrochloric acid (3.1) once more, then take up the residue with water, heat to complete the dissolution of the salts, transfer quantitatively to a 1 000 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 1 mg of nickel (Ni).

3.12.2 Weigh, to the nearest 0,001 g, 6,730 g of nickel ammonium sulphate $[(NH_4)_2SO_4NiSO_4.6H_2O]$. Dissolve in water, transfer the solution quantitatively to a 1 000 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 1 mg of nickel (Ni).

3.13 Nickel, 0,1 g/l standard solution.

Transfer 100,0 ml of standard nickel solution (3.12), to a 1 000 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 0,1 mg of nickel (Ni).

3.14 Nickel, 0,005 g/l standard solution.

Transfer 50,0 ml of standard nickel solution (3.13), to a 1 000 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 0,005 mg of nickel (Ni).

Prepare this standard solution at the moment of use.

3.15 Bromothymol blue, 1 g/l solution in ethanol.

Dissolve 0,1 g of bromothymol blue in 5 ml of 95 % (*V/V*) ethanol, make up the volume to 100 ml with water and mix.

4 APPARATUS

Usual laboratory apparatus, and

4.1 Spectrophotometer, or

4.2 Electrophotometer.

5 SAMPLING

5.1 Laboratory sample[1)]

5.2 Test sample

Chips not more than 1 mm thick shall be obtained by milling or drilling.

6 PROCEDURE

6.1 Test portion

Weigh, to the nearest 0,001 g, about 1 g of the test sample (5.2).

6.2 Blank test

Carry out a blank test in parallel with the analysis, following the same procedure and using the same quantities of all reagents as are used in the analysis.

6.3 Preparation of the calibration curve

6.3.1 *Preparation of standard matching solutions,* related to photometric measurements carried out with an optical path length of 2 cm

Into a series of seven 50 ml volumetric flasks, transfer the volumes of standard nickel solution (3.14) indicated in table 1.

TABLE 1

Volume of standard nickel solution (3.14)	Corresponding mass of nickel (Ni)
ml	mg
0 *	0
1,0	0,005
2,0	0,010
5,0	0,025
10,0	0,050
15,0	0,075
20,0	0,100

* Compensation solution.

Then add to each volumetric flask 20 ml of hydrochloric acid (3.10) and the quantity of water necessary to obtain about 40 ml.

[1)] Sampling from supply lots will be the subject of a future International Standard.

6.3.2 *Colour reaction*

Add 1 ml of bromine water (3.11) and wait for at least 15 min. Add slowly, while stirring, ammonia solution (3.6) until the colour disappears and then add an excess of 2 ml.

Cool the solution to a temperature below 30 °C. Finally, add 2 ml of dimethylglyoxime solution (3.7), make up to volume and mix.

6.3.3 *Photometric measurements*

Measure the absorbance of each solution after 10 min, but not more than 30 min, using the spectrophotometer (4.1) at the maximum of the absorption curve (wavelength approximately 445 nm) or with the electrophotometer (4.2) fitted with suitable filters, after having adjusted the apparatus to zero absorbance against the compensation solution.

6.3.4 *Plotting of the calibration curve*

Plot a graph showing, for example, the amounts of nickel (Ni), expressed in milligrams, contained in 50 ml of standard matching solution as abscissae, and the corresponding absorbance values as ordinates.

6.4 Determination

6.4.1 *Preparation of the test solution*

Transfer the test portion (6.1) to a beaker of suitable capacity (for example 250 ml), and cover it with a watch glass. Add 25 ml of water and, in small portions, 7,5 ml of hydrochloric acid (3.1) and 2 ml of nitric acid (3.2). Once the reaction is finished, heat to boiling and boil for 2 or 3 min. Filter if necessary. Allow to cool to ambient temperature. According to the presumed nickel content, operate on the whole of the test solution or, having brought the volume of this solution up to 100 ml, operate on the aliquot indicated in table 2.

TABLE 2

Presumed nickel content	Volume of the test solution	Volume of aliquot of the test solution for the colour reaction	Quantity of nickel present
% (*m*/*m*)	ml	ml	mg
from 0,000 5 to 0,01	–	whole	from 0,005 to 0,10
from 0,01 to 0,02	100	50,0	from 0,05 to 0,10
from 0,02 to 0,05	100	20,0	from 0,04 to 0,10

Transfer the aliquot of the test solution to a beaker of suitable capacity (for example 250 ml). In all cases bring the volume of the solution to about 40 ml by evaporation or dilution. Add 5 ml of hydroxylammonium chloride solution (3.3), 20 ml of citric acid solution (3.4), 10 ml of thiourea solution (3.5) and 3 to 5 drops of bromothymol blue solution (3.15). Add slowly the ammonia solution (3.6) until the indicator turns blue and then add an excess of 0,5 ml. Add 5 ml of dimethylglyoxime solution (3.7) and transfer the solution quantitatively to a separating funnel of suitable capacity (for example 200 ml). Cool the solution before extraction.

6.4.2 *Extraction of the nickel-dimethylglyoxime complex*

Add to the separating funnel 10 ml of chloroform (3.8) and shake carefully for 1 min. Allow to settle, draw off the organic phase and collect it in a second separating funnel of suitable capacity (for example 100 ml). Add to the funnel containing the aqueous phase 1 or 2 ml of chloroform (3.8) and, without shaking, draw off the organic phase and add it to that contained in the second separating funnel. Add once more to the aqueous phase 5 ml of chloroform (3.8), shake for 30 s, allow to settle, draw off the organic phase and collect it in the second separating funnel, proceeding as already indicated. Discard the aqueous phase. Add to the organic phase 20 ml of ammonia solution (3.9) and shake for 30 s. Allow to settle, draw off the organic phase and place it in a third separating funnel of suitable capacity (for example 100 ml), washing with 1 or 2 ml of chloroform (3.8). Add to the funnel containing the aqueous phase 5 ml of chloroform (3.8) and shake for 30 s.

Allow to settle, draw off the organic phase and add it to that contained in the third funnel. Discard the aqueous phase.

6.4.3 *Passage of the nickel complex into aqueous solution*

Add to the separating funnel containing the organic phase 10 ml of hydrochloric acid (3.10) and shake, carefully, for 1 min, allow to settle, draw off the organic phase and collect it in another separating funnel of suitable capacity (for example 100 ml). Add to the funnel containing the aqueous phase 1 or 2 ml of chloroform (3.8) and, without shaking, draw it off and add to the funnel containing the organic phase. Repeat once more the treatment of the organic phase with 10 ml of hydrochloric acid (3.10), still collecting the aqueous phase in the same separating funnel. Discard the organic phase.

Add to the aqueous phase 5 ml of chloroform (3.8) and shake for 30 s. Allow to settle, draw off carefully the organic phase and discard it. Continue according to the procedure described in 6.3.2.

6.4.4 *Photometric measurements*

Measure the absorbance of each solution after 10 min but not more than 30 min, using the spectrophotometer (4.1) at the maximum of the absorption curve (wavelength approximately 445 nm) or with the electrophotometer (4.2) fitted with suitable filters, after having adjusted the apparatus to zero absorbance against the compensation solution.

7 EXPRESSION OF RESULTS

By means of the calibration curve (see 6.3.4), determine the quantity of nickel corresponding to the value of the photometric measurement. The content of nickel (Ni) is given, as a percentage by mass, by the formula :

$$\frac{(m_1 - m_2) \times D}{10 \times m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in milligrams, of nickel found in the test solution or in the aliquot of the test solution;

m_2 is the mass, in milligrams, of nickel found in the corresponding blank test solution or in the aliquot of the blank test solution;

D is the ratio of the volume of the test solution to the volume of the aliquot taken for the colour reaction.

8 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the form in which they are expressed;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or regarded as optional.