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Aluminium and aluminium alloys — Determination of nickel — Spectrophotometric method using dimethylglyoxime

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FOREWORD

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INTERNATIONAL STANDARD

ISO 3979-1977 (E)

Aluminium and aluminium alloys — Determination of nickel — Spectrophotometric method using dimethylglyoxime

1 SCOPE

This International Standard specifies a spectrophotometric method using dimethylglyoxime for the determination of nickel in aluminium and aluminium alloys.

2 FIELD OF APPLICATION

The method is applicable to nickel (Ni) contents between 0,001 and 3 % (*m/m*).

3 PRINCIPLE

Attack of a test portion by a solution of hydrochloric acid, in the presence of a small quantity of iron, to bring about the precipitation of the nickel, and filtration of the residue.

Dissolution of the residue, which contains all the nickel, by an acid mixture and complexing of the interfering elements by the addition, at a given pH value, of tartaric acid, hydroxylammonium chloride and sodium thiosulphate.

Formation of the nickel-dimethylglyoxime complex, extraction of this complex by chloroform and 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 an ammoniacal medium.

Photometric measurement of the coloured complex at the maximum of the absorption curve (wavelength about 445 nm).

4 REAGENTS

Throughout the analysis use only reagents of analytical grade and only distilled water or water of equivalent purity.

4.1 Chloroform ($CHCl_3$), ρ about 1,48 g/ml.

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

4.3 Hydrofluoric acid, ρ about 1,05 g/ml, solution about 40 % (*m/m*).

4.4 Ammonia solution, ρ about 0,90 g/ml, 27 % (*m/m*) solution or about 14,4 N.

4.5 Ammonia solution, ρ about 0,99 g/ml, 0,85 % (*m/m*) solution or about 0,5 N.

Dilute 35 ml of ammonia solution (4.4), make up the volume to 1 000 ml and mix.

4.6 Sulphuric acid, ρ about 1,48 g/ml, 58 % (*m/m*) solution or about 18 N.

Add to about 400 ml of water, while stirring and cooling, 500 ml of sulphuric acid solution, ρ about 1,84 g/ml [solution about 96 % (*m/m*)].

After cooling, make up the volume to 1 000 ml and mix.

4.7 Hydrochloric acid, ρ about 1,1 g/ml, 20 % (*m/m*) solution or about 6 N.

Dilute 500 ml of hydrochloric acid solution, ρ about 1,19 g/ml, solution about 38 % (*m/m*), with water, make up the volume to 1 000 ml and mix.

4.8 Hydrochloric acid, ρ about 1,03 g/ml, 7,1 % (*m/m*) solution or about 2 N.

Dilute 170 ml of hydrochloric acid solution, ρ about 1,19 g/ml, 38 % (*m/m*) solution or about 12 N, with water, make up the volume to 1 000 ml and mix.

4.9 Hydrochloric acid, ρ about 1,01 g/ml, 1,81 % (*m/m*) solution or about 0,5 N.

Dilute 250,0 ml of hydrochloric acid solution (4.8), make up the volume to 1 000 ml and mix.

4.10 Tartaric acid, 300 g/l solution.

Dissolve 300 g of tartaric acid ($C_4H_6O_6$) in water and heat to assist dissolution. Filter, if necessary, through a medium textured filter and collect the filtrate in a 1 000 ml volumetric flask. Wash with water and, after cooling to ambient temperature, make up to volume and mix.

4.11 Acid mixture

Mix, in a conveniently sized receptacle, 200 ml of the nitric acid solution (4.2) with 50 ml of the hydrochloric acid solution (4.7).

4.12 Bromine water, solution saturated at ambient temperature.

4.13 Hydrogen peroxide, about 30 % (*m/m*) solution.

4.14 Sodium hydroxide, 250 g/l solution, about 6,25 N.

In a nickel capsule, dissolve 250 g of sodium hydroxide (NaOH) in water. After cooling, make up the volume to 1 000 ml and mix. Transfer the solution immediately to a plastics container.

4.15 Sodium hydroxide, 2 g/l solution, about 0,05 N.

Dilute 8 ml of the sodium hydroxide solution (4.14), make up the volume to 1 000 ml and mix.

4.16 Iron(III) chloride, solution corresponding to 1 g of Fe per litre.

Dissolve 0,48 g of $FeCl_3.6H_2O$ (or 0,3 g of $FeCl_3$) in 5 ml of the hydrochloric acid solution (4.7), make up the volume to 100 ml and mix.

4.17 Hydroxylammonium chloride, 100 g/l solution, freshly prepared.

Dissolve in water, 2,5 g of hydroxylammonium chloride ($NH_2OH.HCl$) make up the volume to 25 ml and mix.

4.18 Sodium thiosulphate, 500 g/l solution.

Dissolve 500 g of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in recently boiled hot water. Heat to assist the dissolution of the salt, filter through a close textured filter and collect the filtrate in a 1 000 ml volumetric flask. Wash with recently boiled hot water, cool to ambient temperature, make up the volume with recently boiled water and cool to ambient temperature. Mix.

4.19 Dimethylglyoxime, 10 g/l solution in ethanol.

Dissolve 1 g of dimethylglyoxime ($C_4H_8O_2N_2$) in 95 % (*V/V*) ethanol, make up the volume to 100 ml with the same ethanol and mix.

4.20 Nickel, 1 g/l standard solution.

Prepare this solution according to one of the following methods :

4.20.1 Weigh, to the nearest 0,000 1 g, 1 g of pure nickel (titre greater than or equal to 99,7 %) and transfer to a tall-form beaker of suitable capacity (800 to 1 000 ml, for example). Cover with a watch glass and add 10 ml of water and 10 ml of the nitric acid solution (4.2). Allow the nickel to react slowly, heating moderately to complete the attack. Once the reaction is finished, add 10 ml of hydrochloric acid, ρ about 1,19 g/ml [38 % (*m/m*) solution or about 12 N], and evaporate, carefully, to dryness (do not calcinate).

Repeat once more the treatment with hydrochloric acid, then take up the residue with water, heat to complete the dissolution of the salt and transfer quantitatively to a 1 000 ml volumetric flask. After cooling to ambient temperature, make up to volume and mix.

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

4.20.2 Weigh, to the nearest 0,001 g, 6,730 g of ammonium nickel sulphate [$(NH_4)_2SO_4.NiSO_4.6H_2O$)]. 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).

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

Transfer 100,0 ml of the standard nickel solution (4.20) 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).

4.22 Nickel, 0,01 g/l standard solution.

Transfer 100,0 ml of the standard nickel solution (4.21) to a 1 000 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 0,01 mg of nickel (Ni).

Prepare this standard solution at the moment of use.

5 APPARATUS

Usual laboratory equipment and

5.1 pH meter, fitted with a glass electrode or a combined glass electrode.

5.2 Spectrophotometer.

6 SAMPLING

6.1 Laboratory sample[1]

6.2 Test sample

Chips 1 mm thick or less shall be obtained by milling or drilling.

7 PROCEDURE

7.1 Test portion

Weigh, to the nearest 0,001 g, about 1 g of the test sample (6.2).

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[1] The sampling of aluminium and aluminium alloys will form the subject of a future International Standard.

7.2 Blank test

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

7.3 Establishment of the calibration curve

7.3.1 *Preparation of the reference solutions*

To a series of eight beakers of suitable capacity (150 ml for example) transfer the volumes of standard nickel solution (4.22) indicated in table 1.

TABLE 1

Volume of standard nickel solution (4.22)	**Corresponding mass of nickel**
ml	µg
0 *	0
0,50	5
1,0	10
2,0	20
5,0	50
10,0	100
20,0	200
40,0	400

* Blank test of the reagents used for the calibration curve.

Then add, to each beaker, first the quantity of water necessary to obtain about 40 ml, then 10 ml of the tartaric acid solution (4.10) and 5 ml of the hydroxylammonium chloride solution (4.17).

For each solution separately, and checking with the aid of the pH meter (5.1), add, while stirring, the quantity of sodium hydroxide solution (4.14) necessary to bring the value of the pH to about 4,5 to 5. Then add 10 ml of the sodium thiosulphate solution (4.18) and, while stirring, adjust the value of the pH to 6,5 using first the sodium hydroxide solution (4.14) and then the sodium hydroxide solution (4.15). Remove from the solution the electrodes (or the combined glass electrode), wash with as little water as possible and add the washings to the solution.

Transfer the solutions quantitatively to separating funnels of suitable capacity (250 ml for example), washing with as little water as possible.

7.3.2 *Extraction of the nickel-dimethylglyoxime complex*

Treat each of the solutions contained in the separating funnels as described in 7.3.2 to 7.3.4.

Add to the separating funnel 5 ml of the dimethylglyoxime solution (4.19), mix, add 10 ml of the chloroform (4.1) and shake carefully for 2 min. Allow to settle, draw off the organic phase and collect it in a second separating funnel of suitable capacity (100 ml for example), washing with 1 or 2 ml of the chloroform (4.1). (More precisely add to the separating funnel which contains the aqueous phase 1 or 2 ml of the chloroform (4.1) and, without shaking, draw them off and add to the separating funnel which contains the organic phase).

Add once more to the aqueous phase 5 ml of the chloroform (4.1), shake for 30 s, allow to settle, draw off the organic phase and collect it in the same (second) separating funnel which already contains the organic phase and wash with 1 or 2 ml of the chloroform (4.1), as already indicated. Repeat once more the extraction with 5 ml of chloroform (4.1) and discard the aqueous phase.

Add to the organic phase, collected in the second separating funnel, 20 ml of the ammonia solution (4.5) and shake for 30 s. Allow to settle, draw off the organic phase and place it in a third separating funnel of suitable capacity (100 ml for example), washing with 1 or 2 ml of the chloroform (4.1). Keep the aqueous phase in the second separating funnel.

To the third funnel, which contains the organic phase, add another 20 ml of the ammonia solution (4.5), shake for 30 s and, after it has settled, draw off the organic phase and place it in a fourth separating funnel of suitable capacity (100 ml for example), washing with 1 or 2 ml of the chloroform (4.1). Transfer the aqueous phase to the second separating funnel, which already contains the aqueous phase from the first washing, wash the third funnel with 5 ml of the chloroform (4.1) and transfer to the aqueous phase collected in the second separating funnel. Shake for 30 s and allow to settle. Draw off the chloroform used for the washing and add to the organic phase collected in the fourth separating funnel, washing with 1 or 2 ml of the chloroform (4.1). Discard the aqueous phase.

7.3.3 *Passage of the nickel complex into aqueous solution*

Add to the separating funnel (fourth) containing the organic phase, 20 ml of the hydrochloric acid solution (4.9) and shake carefully for 30 s. Allow to settle, draw off the organic phase and place it in a fifth separating funnel of suitable capacity (100 ml for example), washing with 1 or 2 ml of the chloroform (4.1). Keep the aqueous phase in the fourth separating funnel. Repeat twice more the treatment of the organic phase with 10 ml of the hydrochloric acid solution (4.9). After each treatment, allow to settle, draw off the organic phase into another separating funnel (sixth and seventh), washing with 1 or 2 ml of the chloroform (4.1) and always collecting the aqueous phase in the fourth separating funnel. After the third treatment discard the organic phase.

Add to the aqueous phase (collected in the fourth funnel) 5 ml of the chloroform (4.1) and shake for 30 s. Allow to settle, draw off the organic phase and discard it. Repeat once more the treatment of the aqueous phase with 5 ml of the chloroform (4.1) and, after it has settled, draw off with care the organic phase and discard it.

7.3.4 *Development of the colour*

Transfer the aqueous phase quantitatively to a 100 ml volumetric flask, washing carefully with water. Add 10 ml of the hydrochloric acid solution (4.8) and bring the volume to about 80 ml. Heat to 35 to 40 °C and add, drop by drop while stirring, bromine water solution (4.12) until an orange colour appears (about 1 ml); then add an excess of about 0,5 ml of bromine water solution (4.12). Allow to cool, and add slowly, while stirring, the ammonia solution (4.4) until the colour disappears (about 2,5 to 2,8 ml) and then add an excess of 1 ml.

Cool the solution to ambient temperature, add 1 ml of the dimethylglyoxime solution (4.19), make up to volume and mix.

7.3.5 *Photometric measurements*

Measure the absorbance of each solution after 10 min, without however exceeding 30 min, using the spectrophotometer (5.2) at the maximum of the absorption curve (wavelength about 445 nm), after having adjusted the apparatus to zero absorbance against the compensating solution.

7.3.6 *Plotting of the curve*

Plot a graph, showing, for example, on the abscissa the values, expressed in milligrams, of the quantities of nickel contained in 100 ml of the reference solution and on the ordinate the corresponding absorbance values.

7.4 Determination

7.4.1 *Preparation of the test solution*

Place the test portion (7.1) in a beaker of suitable size (400 ml for example) and cover with a watch glass. Add, in small portions, cooling if necessary, 25 ml of the hydrochloric acid solution (4.7). Wait until the reaction subsides and heat gently to complete the dissolution; add a small quantity (from a few drops to a few millilitres) of the hydrogen peroxide solution (4.13) and then heat to eliminate the excess of hydrogen peroxide and to complete, if need be, the dissolution of the test portion. Rinse the walls of the beaker and the watch glass with hot water, collecting the washings in the same beaker, dilute to about 80 ml with hot water and filter through a close textured filter. Wash the filter and the residue with hot water and collect the filtrate and the washings in a beaker of suitable size (400 ml for example). Keep this solution.

Transfer the filter with the residue to a platinum crucible, dry and then heat carefully until combustion of the filter (the temperature should not exceed about 600 °C). After cooling, transfer to the crucible 1 to 2 ml of the sulphuric acid solution (4.6), 5 ml of the hydrofluoric acid solution (4.3) and finally, drop by drop, the nitric acid solution (4.2) until a clear solution is obtained. Evaporate this solution until the white sulphuric acid fumes have been completely eliminated and then heat for about 10 min (the temperature should not exceed about 700 °C). Allow to cool, then take up with a few millilitres of hot water and 1 to 2 ml of the hydrochloric acid solution (4.7). Heat gently, add the solution obtained to the test solution and adjust the volume to about 150 ml. Add 0,5 ml of the iron(III) chloride solution (4.16)[1] and 45 ml of the sodium hydroxide solution (4.15). Cover the beaker with a watch glass, heat the solution to 70 to 90 °C and keep the solution at this temperature for 20 min without boiling; finally, boil the solution for 2 to 3 min.

Filter the residue through a sintered glass crucible of suitable porosity (from 15 to 40 µm for example) and wash immediately, with hot sodium hydroxide solution (4.15), the residue and the beaker so as to collect in the crucible any residue which may adhere to the walls of the beaker. Dissolve the residue on the crucible with 10 ml of the hot acid mixture (4.11) diluted at the moment of use with 10 ml of hot water, wash carefully with hot water and collect the filtrate and the washings in the beaker used for the attack of the test portion. Heat to complete the dissolution of the salts, cool to ambient temperature and transfer the solution quantitatively to a 200 ml or 500 ml volumetric flask, according to the expected nickel content. Make up to volume and mix.

7.4.2 *Taking of the aliquot*

According to the expected nickel content, for the volume of the test solution (7.4.1), the volume of the aliquot of the test solution to be taken and the possible dilution, the taking of the aliquot for the colour reaction, follow the indications given in table 2 .

To a beaker of suitable capacity (150 ml for example), transfer the aliquot of the test solution and bring the volume to about 40 ml by concentration or dilution. Add 10 ml of tartaric acid solution (4.10) and 5 ml of the hydroxylammonium chloride solution (4.17). Add, while stirring and checking with the aid of the pH meter (5.1), the quantity of the sodium hydroxide solution (4.14) necessary to bring the value of the pH to about 4,5 to 5. Finally add 10 ml of the sodium thiosulphate solution (4.18) and, while stirring, adjust the value of the pH to 6,5 using first the sodium hydroxide solution (4.14) and then the sodium hydroxide solution (4.15). Remove from the solution the electrodes (or the combined glass electrode), wash with as little water as possible and add the washings to the solution.

Transfer the solution quantitatively to a separating funnel of suitable capacity (250 ml for example), washing with as little water as possible. Continue according to the procedure described in 7.3.2 to 7.3.4.

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[1] The addition of iron(III) chloride solution is not necessary if the iron content of the alloy is over about 0,2 %.

TABLE 2

Expected nickel content	Volume of the test solution (A) (7.4.1)	Aliquot of the test solution (A) to be taken	Volume of the dilution of the aliquot taken (B)	Volume of the aliquot of solution A or B, taken for the colour reaction	Mass of nickel present in the coloured solution
% (*m*/*m*)	ml	ml	ml	ml	µg
from 0,001 to 0,07	200	100,0	–	100,0 (A)	from 5 to 350
from 0,07 to 0,15	200	50,0	–	50,0 (A)	from 175 to 375
from 0,15 to 0,4	200	20,0	–	20,0 (A)	from 150 to 400
from 0,4 to 1	500	20,0	–	20,0 (A)	from 160 to 400
from 1 to 2	500	50,0	250,0	50,0 (B)	from 200 to 400
from 2 to 3	500	50,0	250,0	25,0 (B)	from 200 to 300

7.4.3 *Photometric measurements*

Carry out the photometric measurements on the test solution and the blank test solution after 10 min, without however exceeding 30 min, according to the procedure described in 7.3.5, having adjusted the apparatus to zero absorbance against water.

8 EXPRESSION OF RESULTS

By means of the calibration curve (see 7.3.6), determine the quantity of nickel corresponding to the values of the photometric measurements.

The nickel (Ni) content 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 aliquot of the test solution;

m_2 is the mass, in milligrams, of nickel found in the corresponding 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.

9 TEST REPORT

The test report shall include the following information :

a) the reference of the method used;

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

c) any particular details noted during the test;

d) any operations not specified in this International Standard or any optional operations.