IS 13318 (1992): Spectrophotometric determination of nickel - Test [CHD 1: Inorganic Chemicals]

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भारतीय मानक

स्पैकट्रम प्रकाशमिति द्वारा निकिल ज्ञात करने की पद्धति

Indian Standard

SPECTROPHOTOMETRIC DETERMINATION OF NICKEL — TEST

UDC 543·42 : 546·74

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Chemical Standards Sectional Committee, CHD 001

FOREWORD

This Indian Standard was adopted by the Bureau of Indian Standards, after the draft finalized by the Chemical Standards Sectional Committee had been approved by the Chemical Division Council.

Nickel in the concentration range 5 to 100 ppm in different materials may be determined spectrophotometrically. Many reagents give sensitive colour reaction with nickel but by far the most widely accepted is dimethyl glyoxime. Other related oximes have been claimed to be superior in sensitivity or other properties and procedures employing them are proposed in particular, furildioxime is somewhat more sensitive and may offer advantages in special cases. For all practical purposes, however, the dimethyl glyoxime spectrophotometric method is one of the choices and is more frequently specified than any other method.

The spectrophotometric mothod is based on the strong wine red or brown colour obtained when dimethyl glyoxime is added to a basic solution of nickel which has been treated with an oxidizing agent such as bromine or persulphate (peroxydisulphate).

The photometric method is best applied after the separation of nickel dimethyl glyoxime with chloroform extraction which removes almost all interferences. The separation can be avoided in some specific materials where the nature of interference is known.

In the preparation of this standard, considerable assistance has been derived from Annual Book of ASTM Standards Part 12 Chemical Analysis of Metals and Metal bearing Ores.

In reporting the result of a test or analysis made in accordance with this standard, if the final value observed or calculated, is to be rounded off. it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard
SPECTROPHOTOMETRIC DETERMINATION OF NICKEL — TEST

1 SCOPE

This standard prescribes spectrophotometric method for determination of nickel using dimethyl glyoxime.

2 REFERENCES

The following Indian Standards are the necessary adjuncts to this standard:

IS No.	*Title*
264 : 1976	Specification for nitric acid (*second revision*)
265 : 1987	Specification for hydrochloric acid (*third revision*)
266 : 1977	Specification for sulphuric acid (*second revision*)
1070 : 1977	Specification for water for general laboratory use (*second revision*)
10332 : 1982	Specification for hydrofluoric acid, aqueous

3 QUALITY OF REAGENTS

Unless specified otherwise, pure chemicals and distilled water (*see* IS 1070 : 1977) shall be used in tests.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the result of analysis.

4 OUTLINE OF THE METHOD

4.1 This method is based on the strong wine red or brown colour obtained when dimethyl glyoxime is added to a basic solution of nickel salt which has been treated with an oxidising agent such as bromine. The absorbance of the coloured complex is measured at 540 nm and nickel estimated from calibration curve.

4.2 In the method using bromine as oxidizing agent in ammonical solution, even though the colour intensity varies with time, reproducible values may be obtained, if absorption readings are made within 10 minutes of mixing. For below 1 percent of nickel in iron and steel by this method the error does not exceed 0.02 percent. In aluminium alloy the procedure may be satisfactorily applied to determine nickel from 0.02 to 2 percent. Nickel may be accurately determined in the presence of iron (200 mg) manganese (100 mg) and copper (5 mg) using persulphate as an oxidizing agent.

5 PREPARATION OF SAMPLE SOLUTION

5.1 Metals and Alloys

5.1.1 *Iron and Steel*

5.1.1.1 *Reagents*

a) *Concentrated sulphuric acid* – *See* IS 266 : 1977
b) *Nitric acid* (1: 1) – *See* IS 264 : 1976.
c) *Phosphoric acid* – 85 percent.
d) *Hydrochloric acid* (1 : 1) – *See* IS 265 : 1987.

5.1.1.2 *Procedure*

Dissolve 0.25 g of sample of ordinary steel in 10 ml of 1 : 1 nitric acid and heat until oxides of nitrogen are expelled. For alloy steels dissolve with 20 ml of acid mixture containing 135 ml of concentrated sulphuric acid and 165 ml of 85 percent phosphoric acid per litre. Then add 10 ml of 1 : 1 nitric acid and heat until oxides of nitrogen are expelled. For stainless steel type steels addition of up to 10 ml of 1 : 1 hydrochloric acid will facilitate solution. Finally transfer to a volumetric flask of suitable size and dilute to the mark with water. Use aliquot for developing colour.

5.1.2 *Manganese Steel*

5.1.2.1 *Reagents*

a) *Concentrated nitric acid* – *See* IS 264 : 1976.
b) *Perchloric acid* – 20 percent.
c) *Nitric acid* (1 : 1) – *See* IS 264 : 1976.
d) *Concentrated hydrochloric acid* – *See* IS 265 : 1987.

5.1.2.2 *Procedure*

Treat 1 g of sample with 30 ml of concentrated nitric acid and evaporate to dryness. Add 20 ml of concentrated nitric acid and 5 ml of 20 percent chloric acid. Boil for 5 minutes, and again add the same amount of reagents. Boil for 5 minutes, cool and filter by suction through asbestos and wash, the precipitate of manganese dioxide with 1 : 1 nitric acid. Evaporate the filtrate and washings nearly to dryness; add 10 ml of concentrated hydrochloric acid and dilute to a known volume. Use an aliquot.

5.1.3 *Copper Metal*

5.1.3.1 *Reagents*

a) *Nitric acid* (1 : 1) – *See* IS 264 : 1976.
b) *Nitric acid* – 2 percent.

5.1.3.2 *Procedure*

Weigh accurately a sample depending on the percentage of nickel present and transfer it to a 250 ml beaker and dissolve with 20 ml of 1 : 1 nitric acid. Expel nitrous fumes and transfer it to a 100 ml volumetric flask if the solution is clear and dilute to the mark. If any turbidity, dilute the solution, allow to settle and filter through Whatman No. 42 filter paper and wash the precipitate with 2 percent nitric acid and collect the filtrate and washings into a suitable volumetric flask and dilute to the mark. Use aliquot depending on the concentration of nickel present.

5.1.4 *Copper Alloys, Bronze, Brass*

5.1.4.1 *Reagents*

a) *Nitric acid* (1 : 1) – *See* IS 264 : 1976.
b) *Nitric acid* – 2 percent.

5.1.4.2 *Procedure*

Weigh 1 g of sample and transfer it to a 250 ml beaker. Treat with 20 ml of 1 : 1 nitric acid. After removal of nitrous fumes reduce the volume to 5 ml; dilute and keep overnight. Filter the meta stannic acid by means of Whatman No. 42 filter paper. Wash the precipitate using 2 percent nitric acid. Collect the filtrate and washings in another beaker. Electrolyse the solution to separate copper and lead. Dilute the solution to a known volume after removal of copper and lead. Determine nickel in an aliquot.

5.1.5 *Aluminium Alloys*

5.1.5.1 *Reagents*

a) *Sodium hydroxide* – 30 percent.
b) *Concentrated hydrochloric acid* – *See* IS 265 : 1987.
c) *Concentrated nitric acid* – *See* IS 264 : 1976.

5.1.5.2 *Procedure*

Transfer 1 g of the sample containing 0.002 to 0.05 mg. of nickel to a 250 ml beaker. Add 10 ml of water and dissolve the sample by incremental addition of 20 ml of 30 percent aqueous sodium hydroxide solution until the reaction ceases. Dilute to 100 ml with hot water, filter through Whatman No. 42 filter paper and wash with hot water. Dissolve the residue into the original beaker using a mixture of 10 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid, washing with hot water. Evaporate to approximately 50 ml, cool and dilute to 100 ml. Use aliquot for nickel determination.

5.1.6 *Beryllium Alloys*

5.1.6.1 *Reagents*

a) *Concentrated sulphuric acid* – *See* IS 266 : 1976.
b) *Sulphuric acid* – 1:1
c) *Concentrated nitric acid* – *See* IS 264 : 1976.
d) *Hydrofluoric acid* – *See* IS 10332 : 1982.
e) *Potassium pyrosulphate*

5.1.6.2 *Procedure*

Transfer 1 g of material to a 600 ml beaker, and add 100 ml water and slowly add 20 ml of 1 : 1 sulphuric acid to dissolve the sample. After the reaction has ceased, carefully evaporate to fumes of sulphur trioxide. Cool and wash down the sides of the beaker with water. Add 10 ml of water and heat to dissolve the soluble salts. Filter through Whatman No. 42 filter paper into a 250 ml volumetric flask and wash the paper free of acid with hot water. Ash the paper and residue in a platinum crucible at 600 °C. Treat the residue with 5 to 6 drops of concentrated sulphuric acid, 2 to 3 drops of concentrated nitric acid and 2 to 3 drops of hydrofluoric acid. Then carefully heat to dryness in order to volatilise any silica present. Fuse the residue with 10 g of potassium pyrosulphate, dissolve and cool melt in water. Add this solution to the original filtrate in the 250 ml volumetric flask dilute to volume with water and mix thoroughly. Take an aliquot for extraction and colour development.

5.1.7 *Nickel Chromium Alloys*

5.1.7.1 *Reagents*

a) *Nitric acid* – 1 : 3
b) *Perchloric acid* – 70 percent.

5.1.7.2 *Procedure*

Dissolve 1 g of sample in a 250 ml beaker with 5 ml of 1 : 3 nitric acid and 20 ml of 70 percent perchloric acid. Evaporate nearly to dryness but do not bake the residue. Add 1 ml more of perchloric acid, dilute with water, filter and dilute to a known volume. Use an aliquot for nickel determination.

5.1.8 *Lead, Tin, Antimony and their Alloys*

5.1.8.1 *Reagents*

a) *Bromine*
b) *Hydrobromic acid*
c) *Perchloric acid* – 60 percent.

5.1.8.2 *Procedure*

Depending on the nickel content transfer up to 2.00 g of sample to a 250 ml beaker. Add up to 20 ml of bromine and hydrobromic acid mixture (1 : 9). Cover and heat gently avoiding excessive loss of bromine until dissolution of the sample is complete. When analysing high tin alloys it may be necessary to add a few more extra drops of bromine to ensure complete dissolution of the sample and oxidation of the tin to the stannic state. When dissolution is completed, add 10 ml of perchloric acid and heat with continuous swirling over an open flame in a well ventilated hood to expel tin and antimony bromides. Add a few drops of nitric acid to destroy the lead bromine if separates. Cover and reflux for a few minutes. Cool, wash down the sides of the beaker with water dilute to about 25 ml, bring to boil and boil gently for a few minutes. Filter, if necessary, transfer the filtrate and washings to 100 ml volumetric flask and dilute to volume.

5.1.9 *Magnesium and Magnesium Alloys*

5.1.9.1 *Reagents*

a) *Concentrated hydrochloric acid* – *See* IS 265 : 1987.

b) *Concentrated nitric acid* – *See* IS 264 : 1976.

5.1.9.2 *Procedure*

Transfer 1 g of the sample to a 250 ml beaker. Add 25 ml of water and dissolve the sample by gradually adding 10 ml of hydrochloric acid and 2 ml of nitric acid. When dissolution is complete cool to room temperature. Transfer the solution to a volumetric flask and dilute to volume. Use suitable aliquot.

5.1.10 *Zirconium and Zirconium Alloys*

5.1.10.1 *Reagents*

a) *Hydrofluoric acid* – *See* IS 10332 : 1982.

b) *Concentrated sulphuric acid* – *See* IS 266 : 1977.

5.1.10.2 *Procedure*

Transfer 1 g of the sample to a platinum beaker add 10 to 15 ml of water and 2 ml of hydrofluoric acid in 0.5 ml portions and cover with a platinum lid. Keep the solution covered except when adding reagents. When the sample is almost dissolved add 10 ml of sulphuric acid. When the initial reaction subsidies, heat the solution gently until dissolution is complete, rinse and remove the platinum cover and boil gently to dense white fumes. Cool and cautiously add 50 to 75 ml of water. Heat gently and swirl if necessary to dissolve the salts present. Transfer the clear cool solution to a 100 ml volumetric flask and dilute to mark with water. Use suitable aliquot for nickel determination.

5.2 Silicates

5.2.1 *Reagents*

a) *Concentrated nitric acid* – *See* IS 264 : 1976.

b) *Sulphuric acid* – 1 : 1.

c) *Hydrofluoric acid* – 48 percent.

d) *Concentrated hydrochloric acid* – *See* IS 265 : 1987.

e) *Sodium citrate* – 10 percent.

f) *Ammonia* – 1 : 1.

g) *One percent sodium citrate*

5.2.2 *Procedure*

Weigh 0.5 g of finely ground sample in a platinum dish. Add 3 ml of 1 : 1 sulphuric acid, 0.5 ml of concentrated nitric acid and 5 ml of 48 percent hydrofluoric acid. Mix and evaporate to fumes of sulphuric acid. Cool, add 2 ml of water, mix and evaporate to fumes. Repeat with 2 to 3 ml of water and evaporate again. Add 1 ml of concentrated hydrochloric acid and 5 ml of water and heat the covered dish on the steambath for 15 minutes to bring all soluble material into solution, a residue of mainly calcium sulphide may remain. Add 10 ml of 10 percent sodium citrate solution and heat on the steambath stirring occasionally for 10 minutes. Cool and nutralise with 1 : 1 ammonium hydroxide against litmus paper then add 1 ml in excess. Filter through a small paper and wash with 5 ml of slightly ammonical 1 percent sodium citrate solution. Transfer to a 50 ml volumetric flask, dilute to volume and mix. Use an aliquot.

5.3 Biological Materials

5.3.1 *Reagents*

a) *Concentrated nitric acid* – *See* IS 264 : 1976.

b) *Perchloric acid* – 60 percent.

5.3.2 *Procedure*

Transfer 1 to 4 g of sample to a 500 ml Kjeldahl flask in a second Kjeldahl flask carry the reagents through the procedure for the reagent blank. Add 40 ml of concentrated nitric acid and boil gently so that nearly all the acid is evaporated in 30 minutes and do not char. Then add 13 ml of 60 percent perchloric acid and boil gently to white fumes. Reduce the heat and continue the digestion, just boiling for 10 to 15 minutes. Cool, dilute with an equal volume of water and filter through sintered glass. Dilute to a convenient volume in a volumetric flask. Use an aliquot.

6 SEPARATION OF NICKEL BY DIMETHYL GLYOXIME CHLOROFORM EXTRACTION

6.1 Reagents

a) *Concentrated Ammonia*

b) *Sodium Citrate* – 10 percent.

c) *Dimethyl Glyoxime One Percent in Ethyl Alcohol.*

d) *Chloroform*

e) *Ammonia* (0.5 *M*) – 1 : 3.

f) *Hydrochloric Acid* – 0.5 *M*.

6.2 Procedure

To an aliquot containing about 50 to 100 ppm of nickel add 5 ml of 10 percent sodium citrate. Neutralise with concentrated ammonia and add a few drops in excess ($pH > 7.5$). Add 2 ml of dimethyl glyoxime (or more as may be required if much copper or cobalt is present, that is, extra volume of 2 ml for each 10 mg of copper and 5 ml for each 10 mg of cobalt). Extract with three 2 to 3 ml portions of chloroform shaking for 30 seconds each time. Shake the combined chloroform extracts with 0.5 ml of 1 : 3 (0.5 *M*) ammonia. Repeat the wash with another portion of ammonia if much copper or cobalt is present. Shake the ammonia washings with 1 or 2 ml of chloroform and add the latter to the chloroform extract. Carry out reagent blank using the same quantity of reagents.

Return the nickel to the ionic state by shaking with two 5 ml portions of 0.5 *M* hydrochloric acid, transfer this solution to a 100 ml volumetric flask and proceed as per **7.1.2**.

7 COLOUR DEVELOPMENT

7.1 Method Using Persulphate for Oxidation

7.1.1 *Reagents*

a) *Sodium citrate* – 10 percent.

b) *Potassium persulphate* – 2 percent.

c) *Sodium hydroxide* – 2 *N*.

d) *Standard nickel solution.*

Dissolve 0.447 9 g of nickel sulphate ($NISO_4 . 6H_2O$) in water or 0.1 g of 99.9 percent pure nickel in 10 ml of nitric acid and when dissolution in complete boil gently to expel oxides of nitrogen and dilute to 1 litre. This solution contains 0.1 mg/ml of nickel and may be further diluted to 0.01 mg/ml, if necessary.

7.1.2 *Calibration*

Transfer 1, 2, 4, 6, 8 and 10 ml of standard nickel solution (1 ml = 0.01 mg Ni) to six 100 ml volumetric flasks. Add 5 ml of 1 *N* hydrochloric acid. Dilute to 50 ml and add 1 ml of 10 percent sodium citrate, 3 ml of 2 percent potassium persulphate solution, 15 ml of 2 *N* sodium hydroxide solution and finally 1 ml of 1 percent ethanolic dimethyl glyoxime solution. Heat to 60 to 70°C and keep at the temperature for 5 minutes. Cool to room temperature and dilute to volume. Measure the absorbance at 465 nm. Plot the photometric readings of the calibration solution against milligrams of nickel present in 100 ml of solution.

7.1.3 *Procedure*

Develop the colour as described under **7.1.2**.

7.2 Method Using Bromine for Oxidation

7.2.1 *Reagents*

a) *Perchloric acid* – 6 percent.

b) *Sodium citrate* – 10 percent

c) *Ammonia* – 1 : 1.

d) *Bromine water.*

e) *Dimethyl glyoxime in ethanol* – 1 percent.

7.2.2 *Calibration*

Transfer 1, 2, 4, 6, 8 and 10 ml of standard nickel solution (1 ml = 0.01 mg) to six 100 ml volumetric flask. add 2 ml of perchloric acid to each flask. Also prepare a separate reference solution by adding 2 ml of perchloric acid to a 100 ml volumetric flask. Dilute to 50 ml and add successively (swirling the flasks between additions) 10 ml of sodium citrate, 5 ml of bromine water and adjust sufficient ammonia (1 : 1) to bleach the bromine colour. Add 3 ml of ammonia (1 : 1) in excess and cool to room temperature. Add 3 ml of dimethyl glyoxime solution dilute to the mark and mix. (The addition of bromine water, ammonia and dimethyl glyoxime should be made without interruption and subsequent photometric measurement should be made after 10 ± 2 minutes after addition of dimethyl glyoxime.) Transfer a suitable quantity of the solution to an absorption, cool and measure the absorbance at 530 nm. Plot the photometric readings of the calibration solution against milligrams of nickel per 100 g of solution.

7.2.3 *Procedure*

Develop the colour as described under **7.2.2** and read the absorbance against reagent blank.

8 CALCULATION

8.1 Convert the absorbance photometric readings of the sample into milligrams of nickel by means of calibration curve. Calculate the percentage of nickel as follows :

$$\text{Nickel, percent by mass} = \frac{A}{B \times 10}$$

where

A = mass of nickel in mg in the sample or aliquot used, and

B = mass of sample in g represented by the sample or aliquot used.

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