

# ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

## ISO RECOMMENDATION R 315

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES  
DETERMINATION OF NICKEL

<https://standards.iteh.ai/catalog/standards/sist/6874ac32-a804-4164-ac41-749495211944/iso-r-315-1963>  
ISO/R 315:1963  
1st EDITION  
July 1963

COPYRIGHT RESERVED

The copyright of ISO Recommendations and ISO Standards belongs to ISO Member Bodies. Reproduction of these documents, in any country, may be authorized therefore only by the national standards organization of that country, being a member of ISO.

For each individual country the only valid standard is the national standard of that country.

Printed in Switzerland

Also issued in French and Russian. Copies to be obtained through the national standards organizations.

## BRIEF HISTORY

The ISO Recommendation R 315, *Methods of Chemical Analysis of Manganese Ores—Determination of Nickel*, was drawn up by Technical Committee ISO/TC 65, *Manganese Ores*, the Secretariat of which is held by the Komitet Standartov, Mer i Izmeritel'nyh Priborov pri Sovete Ministrov SSSR.

Work on this question by the Technical Committee began in 1954 and led, in 1957, to the adoption of a Draft ISO Recommendation.

In October 1958, this Draft ISO Recommendation (No. 248) was circulated to all the ISO Member Bodies for enquiry. It was approved by the following Member Bodies:

iTeh STANDARD PREVIEW  
(standards.iteh.ai)

Austria	Hungary	Republic of
Bulgaria	Ireland	South Africa
Burma	Italy	Romania
Chile	Japan	Spain
Czechoslovakia	Netherlands	United Kingdom
France	Poland	U.S.S.R.
Germany	Portugal	

ISO/R 315:1963  
<https://standards.iteh.ai/catalog/standards/sist/a8a4ac32-9804-4164-ac41-749495211944/iso-r-315-1963>

One Member Body opposed the approval of the Draft: India.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in July 1963, to accept it as an ISO RECOMMENDATION.

## METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

## DETERMINATION OF NICKEL

(Atomic mass Ni: 58.69; molecular mass NiO: 74.69)

This ISO Recommendation contains three parts:

- I. Introduction . . . . . section 1,
- II. Gravimetric method, for nickel content exceeding 0.1 per cent . . . . . sections 2 to 5,
- III. Colorimetric method, for nickel content below 0.1 per cent . . . . . sections 6 to 9.

**iTeh STANDARD PREVIEW**  
(standards.iteh.ai)

## I. INTRODUCTION

ISO/R 315:1963

<https://standards.iteh.ai/catalog/standards/sist/a8a4ac32-a804-4164-ac41-7414>

## 1. GENERAL INSTRUCTIONS

- 1.1 In the following analysis, use a sample for chemical analysis of air-dried manganese ore, which has been crushed to a size not exceeding 0.10 mm and checked on a sieve of appropriate size.

Simultaneously with the collection of samples for the determination of nickel, take three more test samples for the determination of hygroscopic moisture.

Calculate the content of nickel in ore which is absolutely dry by multiplying the numerical results of the determination of nickel by the conversion factor  $K$ , as found from the following formula:

$$K = \frac{100}{100 - A}$$

where

$A$  = hygroscopic moisture content, per cent.

- 1.2 The determination of nickel in manganese ore is carried out by simultaneously analysing three samples of ore, with two blank determinations to enable a corresponding correction in the result of the determination to be made.

Simultaneously and under the same conditions, carry out a check analysis of a standard sample of manganese ore, for nickel content.

The arithmetical mean of the three results is accepted as the final result.

The following conditions should be observed:

The maximum difference between the highest and the lowest results should not exceed double the absolute value of the permissible tolerance on the result of the analysis (for the corresponding interval of nickel content), shown in the tables under clauses 5.2 and 9.2, "Accuracy of method".

The average result of the simultaneous check analysis of the standard sample of manganese ore for nickel content should not differ from the result shown in the certificate by more than the  $\pm$  value of the permissible tolerance (for the corresponding interval of nickel content), shown in the tables under clauses 5.2 and 9.2, "Accuracy of method".

For the analysis, take a standard sample of the type of ore to which the sample being analysed belongs.

1.3 The test samples and the residues should be weighed to an accuracy of  $\pm 0.0002$  g.

1.4 Distilled water should be used during the procedure and for the preparation of solutions.

1.5 Meanings of the following expressions:

hot water (or solution) implies a temperature of the liquid of 60 to 70 °C;

warm water (or solution) implies a temperature of the liquid of 40 to 50 °C;

diluted 1 : 1, 1 : 2, 1 : 5, etc. means that

the first figure gives the number of parts by volume of concentrated acid or some other solution, and the second figure gives the number of parts by volume of water.

ISO/R 315:1963

1.6 Indications as to the concentration of solutions show the quantity of solute (in grammes) in the corresponding volume of the solvent.

1.7 The following symbols and abbreviations are used:

<i>d</i>	relative density
g	gramme
g/l	grammes per litre
ml	millilitre
mm	millimetre
nm	nanometre
PFA	pure for analysis

## II. GRAVIMETRIC METHOD FOR NICKEL CONTENT EXCEEDING 0.1 PER CENT

### 2. PRINCIPLE OF METHOD

The method is based on the precipitation of nickel with dimethyl-glyoxime. Iron, manganese and other elements are converted beforehand into tartrate or citrate complexes.

The precipitate of nickel glyoxime is dried and weighed.

### 3. REAGENTS REQUIRED

- 3.1 *Ammonium hydroxide*, PFA (*d* 0.91).
- 3.2 *Dimethyl-glyoxime*, PFA, alcohol solution (10 g/l).
- 3.3 *Hydrochloric acid*, PFA (*d* 1.19).
- 3.4 *Hydrochloric acid*, PFA, diluted 1 : 1.
- 3.5 *Hydrochloric acid*, PFA, diluted 1 : 5.
- 3.6 *Hydrochloric acid*, PFA, diluted 1 : 20.
- 3.7 *Tartaric (citric) acid*, PFA, solution (250 g/l).
- 3.8 *Hydrofluoric acid*, PFA (40 per cent).
- 3.9 *Sulphuric acid*, PFA (*d* 1.84).
- 3.10 *Sodium carbonate*, PFA, anhydrous.

### 4. PROCEDURE

- 4.1 Weigh 2 g of manganese ore into a 300 ml beaker and dissolve while heating in 25 ml of hydrochloric acid (*d* 1.19). Evaporate the solution until dry, add 10 to 15 ml of hydrochloric acid (*d* 1.19) to the dry residue, and evaporate again to dryness.
- 4.2 Add 10 to 15 ml of hydrochloric acid (*d* 1.19) to the dry residue, dilute with hot water to 30 to 40 ml, boil until salts are dissolved and then filter off the insoluble residue.
- 4.3 Wash the filter and residue 5 or 6 times with hot hydrochloric acid, diluted 1 : 20, and 2 or 3 times with hot water. Place in a platinum crucible, and ignite at a temperature of 500 to 600 °C.
- 4.4 Moisten the residue in the crucible with water, add 1 or 2 drops of sulphuric acid (*d* 1.84) and 5 to 10 ml of hydrofluoric acid (40 per cent), and evaporate until dry. Heat the residue to a temperature of 500 to 600 °C, cool, add 1 to 2 g of anhydrous sodium carbonate, and fuse the mixture at a temperature of 900 to 1000 °C. Extract the fusion with hydrochloric acid, diluted 1 : 5.

- 4.5 Remove the crucible from the beaker, rinsing it beforehand with water, and add the resultant solution to the original filtrate.

Add to the combined solutions 25 ml of the solution of citric or tartaric acid (250 g/l), then add ammonium hydroxide until a slight odour is detected. Dilute with water to 150 to 200 ml, add 10 ml of dimethyl-glyoxime solution, stir carefully and leave standing for from 1 to 2 hours at room temperature.

- 4.6 Filter off the precipitate of nickel glyoxime on a medium filter, wash it with warm water, and then dissolve it in hot hydrochloric acid, diluted 1 : 1, collecting the solution in the beaker in which the precipitation was effected. To dissolve the residue, pour in three portions of 10 ml each of hot hydrochloric acid, diluted 1 : 1, and then wash the filter 3 or 4 times with hot water.
- 4.7 Add 3 ml of the solution of citric acid or tartaric acid (250 g/l) and ammonium hydroxide until a slight odour is detected, adding an excess of 1 ml of ammonia. Pour in 10 ml of the alcohol solution of dimethyl-glyoxime (10 g/l), stir carefully, allow the precipitate to settle for 20 to 30 min, filter off into a weighed sintered glass crucible, and wash 6 to 8 times with warm water. Dry the sintered glass crucible with the precipitate at a temperature of 110 to 120 °C to constant mass.

## 5. EXPRESSION OF RESULTS

### 5.1 Method of calculation

The percentage content of nickel is calculated from the following formula:

$$\text{Ni} = \frac{A \times 0.2032 \times 100}{G} \text{ per cent}$$

where

$A$  = mass of dried residue of nickel glyoxime, in grammes;

$G$  = mass of sample of ore, in grammes;

0.2032 = conversion factor for nickel glyoxime to nickel.

### 5.2 Accuracy of method

The permissible tolerances, per cent (absolute value), are given in the table below:

Nickel content		Permissible tolerance (in absolute value)
from	to	
0.10 per cent	0.30 per cent	± 0.010 per cent
(over) 0.30 per cent	0.50 per cent	± 0.020 per cent

### III. COLORIMETRIC METHOD

#### FOR NICKEL CONTENT BELOW 0.1 PER CENT

#### 6. PRINCIPLE OF METHOD

The method is based on the formation of a coloured soluble complex of nickel with dimethylglyoxime in an alkali medium under the action of one of the following oxidizers: ammonium persulphate, iodine or bromine. As a preliminary step, manganese is separated in the form of a dioxide.

#### 7. REAGENTS REQUIRED

- 7.1 *Ammonium persulphate* ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ), PFA, solution (30 g/l).
- 7.2 *Dimethyl-glyoxime*, PFA, alkaline solution (10 g/l). 1 g of dimethylglyoxime is dissolved in 100 ml of caustic soda solution (50 g/l).
- 7.3 *Potassium bromate* ( $\text{KBrO}_3$ ), PFA.
- 7.4 *Tartaric acid*, PFA, solution (200 g/l).
- 7.5 *Sulphuric acid*, PFA ( $d$  1.84).
- 7.6 *Sulphuric acid*, PFA, diluted 1 : 4.
- 7.7 *Sulphuric acid*, PFA, diluted 1 : 20.
- 7.8 *Hydrofluoric acid*, PFA (40 per cent).
- 7.9 *Potassium pyrosulphate* ( $\text{K}_2\text{S}_2\text{O}_7$ ), PFA.
- 7.10 *Sodium hydroxide*, PFA, solution (50 g/l).
- 7.11 *Hydrogen peroxide*, PFA, 30 per cent (perhydrol).
- 7.12 *Standard solution of nickel*. Dissolve 0.1000 g of metallic nickel, PFA, in 20 ml of hydrochloric acid, diluted 1 : 4, PFA, in the presence of a few drops of nitric acid, PFA ( $d$  1.40). Boil the solution until it ceases to evolve nitric oxides. Pour the whole solution into a measuring flask of 1 litre capacity, add water up to the mark, and mix; 1 ml of the solution contains 0.0001 g of nickel.

#### 8. PROCEDURE

- 8.1 Weigh 1 g of manganese ore into a 300 ml beaker, and dissolve in 30 ml of sulphuric acid, diluted 1 : 4, heating continuously and adding, drop by drop, a 30 per cent solution of hydrogen peroxide until decomposition is complete.
- 8.2 Evaporate the solution until fumes of sulphur trioxide are evolved, cool the solution, dilute with 40 to 50 ml of water, and filter off the insoluble residue.
- 8.3 Wash the filter and the residue 6 to 8 times with hot water, place in a platinum crucible, and ignite to a temperature of 500 to 600 °C. Cool and moisten the residue in the crucible with water, add 1 to 2 drops of sulphuric acid ( $d$  1.84) and 5 to 7 ml of hydrofluoric acid (40 per cent), and evaporate to dryness. Heat the residue to a temperature of 500 to 600 °C; cool, add 2 to 3 g of potassium pyrosulphate, and fuse at 500 to 600 °C. Extract the fusion in 10 to 20 ml of sulphuric acid, diluted 1 : 20, remove the crucible from the beaker, first washing it with water, and add the resultant solution to the original one. Add to the combined solutions 1 g of potassium bromate, heat to boiling, and boil for 5 min.

- 8.4 Filter off the precipitated manganese dioxide on a medium filter, and wash 8 to 10 times with hot water. Discard the filter with the residue. Evaporate the solution until sulphur trioxide fumes are evolved; after cooling the salts, dissolve them in water, and pour the solution thus obtained into a 100 ml measuring flask. Add 10 ml of tartaric acid solution (200 g/l), 30 ml of sodium hydroxide solution (50 g/l), 10 ml of ammonium persulphate solution (30 g/l) and 10 ml of the alkaline solution of dimethyl-glyoxime (10 g/l).
- 8.5 After the addition of each reagent, stir the solution carefully. Allow the solution to stand for 5 to 10 min and develop colour, then add water until it reaches the mark. Stir again, and carry out the colorimetric determination with a blue light-filter (wavelength 420 to 430 nm). In the simultaneous blank test, use 10 ml of sodium hydroxide solution (50 g/l) instead of dimethyl-glyoxime.
- 8.6 The percentage of nickel is determined by the calibration curve method or by the comparison method from the optical density of the solution being tested.

(a) *Calibration curve method*

To construct the calibration curve, take corresponding volumes of the standard solution of nickel, covering both the extreme limits (maximum and minimum) and the intermediate degrees of nickel concentration in the given type of ore, and take them through all the stages of the analysis simultaneously with the sample being analysed.

The percentage of nickel in the sample being analysed is determined, from the calibration curve, on the basis of the optical density of the solution.

(b) *Comparison method*

Take a known volume of the standard solution of nickel of a concentration approaching that of the sample being analysed, and pass it through all the stages of the analysis simultaneously with the sample.

ISO/R 315:1963  
<https://standards.iso.org/standard/54432-a804-4164-ac41-749495211944/iso-r-315-1963>

## 9. EXPRESSION OF RESULTS

### 9.1 Method of calculation

The percentage content of nickel is calculated

- (a) by the calibration curve, graphically,  
 (b) by the comparison method, from the following formula:

$$Ni = \frac{D_x C_{st} \times 100}{D_{st} G} \text{ per cent}$$

- where  $D_x$  = optical density of the solution being analysed;  
 $C_{st}$  = concentration of the standard solution, expressed in grammes of nickel;  
 $D_{st}$  = optical density of the standard solution of nickel;  
 $G$  = mass of sample of ore, in grammes.

### 9.2 Accuracy of method

The permissible tolerances, per cent (absolute value), are given in the table below:

Nickel content		Permissible tolerance (in absolute value)
from	to	
0.01 per cent	0.05 per cent	$\pm 0.003$ per cent
(over) 0.05 per cent	0.10 per cent	$\pm 0.005$ per cent