International Standard ISO 6352

Ferronickel — Determination of nickel content — Dimethylglyoxime gravimetric method

Ferro-nickel — Dosage du nickel — Méthode gravimétrique à la diméthylglyoxime

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Foreword

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International Standard ISO 6352 was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

Ferronickel — Determination of nickel content — Dimethylglyoxime gravimetric method

1 Scope and field of application

This International Standard specifies a gravimetric method for the determination of the nickel content of ferronickel in the range 15 to 60 % (m/m).

2 References

ISO 385/1, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648, *Laboratory glassware — One-mark pipettes.*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks.*

ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests.*

3 Principle

Dissolution of a test portion in nitric acid. Precipitation of silica by dehydration in perchloric acid. Removal of silica by filtration. Precipitation of nickel from a tartro-ammoniacal medium by an ethanolic solution of dimethylglyoxime. A second precipitation of nickel and weighing after drying at 150 °C. Determination of residual nickel in the filtrates by atomic absorption spectrometry.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Acetic acid, ϱ_{20} = 1,05 g/ml, diluted 1 + 1.

4.2 Ammonium hydroxide, ϱ_{20} = 0,925 g/ml.

4.3 Dimethylglyoxime, 10 g/l solution in ethanol.

4.4 Hydrochloric acid, ϱ_{20} = 1,19 g/ml.

4.5 Hydrochloric acid, ϱ_{20} = 1,19 g/ml, diluted 1 + 9.

4.6 Nitric acid, ϱ_{20} = 1,41 g/ml.

4.7 Nitric acid, ϱ_{20} = 1,41 g/ml, diluted 1 + 1.

4.8 Perchloric acid, ϱ_{20} = 1,61 g/ml [72 % (m/m)].

4.9 Tartaric acid, 500 g/l solution.

4.10 Hydrofluoric acid, ϱ_{20} = 1,14 g/ml, diluted 1 + 1.

WARNING — Hydrofluoric acid is extremely irritating and corrosive to skin and mucous membranes, producing severe skin burns which are slow to heal. In case of skin contact, wash well with water and seek medical advice.

5 Apparatus

Ordinary laboratory apparatus, and

5.1 Filtration crucible, fritted glass, of approximately 10 to 20 μm pore diameter.

5.2 Glass beakers, of capacity 600 ml, clean, unetched and flat bottomed.

5.3 Pipettes, of capacities 50 and 100 ml, in accordance with ISO 648, class A.

5.4 Volumetric flasks, of capacities 200 and 1 000 ml, in accordance with ISO 1042, class A.

5.5 Polytetrafluoroethylene (PTFE) beaker, of capacity 600 ml, for samples with a high silicon content.

6 Sampling and samples

6.1 Sampling and preparation of the laboratory sample shall be carried out by normal agreed procedures or, in case of dispute, by the relevant International Standard.

6.2 The laboratory sample normally is in the form of granules, millings or drillings and no further preparation of the sample is necessary.

6.3 If it is suspected that the laboratory sample is contaminated with oil or grease from the milling or drilling process, it shall be cleaned by washing with high purity acetone and drying in air.

6.4 If the laboratory sample contains particles or pieces of widely varying sizes, the test portion should be obtained by riffling.

7 Procedure

WARNING — Fuming perchloric acid is a powerful oxidant and can cause an explosive mixture when in contact with organic materials. All evaporations should be done in fume cupboards suitable for use with perchloric acid.

7.1 Test portion

Weigh, to the nearest 0,001 g, 3,9 to 4,1 g of the laboratory sample and transfer to a 600 ml glass beaker (5.2).

7.2 Blank test

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

7.3 Preparation of crucible

7.3.1 Filter through the crucible (5.1) a hot mixture of 20 ml of hydrochloric acid (4.4), 10 ml of nitric acid (4.6) and 30 ml of water. Wash the crucible with warm water until all the acid has been removed.

7.3.2 Dry the crucible in an oven at 150 °C for 2 h. Cool in a desiccator for 60 min and weigh quickly.

NOTES

1 This procedure is used to condition a new crucible or to clean a used crucible after the analysis is completed.

2 For highest accuracy, the crucible and precipitate (7.5.9) should be weighed, as closely as possible, under the same temperature and humidity conditions as the empty crucible.

7.4 Preparation of test solution

7.4.1 Dissolve the test portion (7.1) by adding 25 ml of water followed by 50 ml of nitric acid diluted 1 + 1. Cover the beaker with a watch-glass and heat gently, if necessary, to complete dissolution.

NOTE — For ferronickel samples containing more than 1 % (m/m) silicon, use a polytetrafluoroethylene beaker (5.5). Attack the test portion by adding successively 25 ml of water, 40 ml of nitric acid (4.7) and 10 ml of hydrochloric acid (4.4). To obtain complete dissolution of the sample, add, at the end of effervescence, 10 ml of hydrofluoric acid (4.10) and 40 ml of perchloric acid (4.8). Heat until evolution of fumes of perchloric acid are obtained. Allow to cool and transfer the solution quantitatively to a glass beaker (5.2). Heat to 260 °C until abundant white fumes of perchloric acid are obtained. Reflux at this temperature for 20 min and proceed as directed in 7.4.2, "Remove the beaker...".

7.4.2 When the metal is dissolved, add 40 ml of perchloric acid (4.8) and heat at 260 °C until abundant white fumes are obtained. Reflux at this temperature for 20 min. Remove the beaker from the hotplate and allow to cool. Add 20 ml of hydrochloric acid (4.4) and 200 ml of warm water. Filter off the silica using a medium porosity filter paper, collecting the filtrate in a 1 000 ml one-mark volumetric flask. Rinse the beaker and wash the silica precipitate three times with hydrochloric acid diluted 1 + 9 and four times with warm water. Discard the silica precipitate, make up the filtrate to the mark with water and mix thoroughly.

7.5 Determination

7.5.1 Pipette from the test solution into a 600 ml beaker, an aliquot containing 60 to 120 mg of nickel, and dilute to 300 ml with water. Use a 100 ml aliquot for samples containing less than 30 % (m/m) nickel and 50 ml for samples containing more than 30 % (m/m) nickel.

7.5.2 Add 10 ml of tartaric acid solution (4.9) to the aliquot (7.5.1). Pour in, while stirring, ammonium hydroxide (4.2) until the colour of the solution changes from yellow to blue-green (pH is slightly alkaline). The solution must remain clear. Restore the yellow colour by slowly adding sufficient acetic acid (4.1). The pH must be between 4 and 5. Heat the solution to 60 °C.

7.5.3 Pour in, while stirring, 4 ml of dimethylglyoxime solution (4.3) for each 10 mg of nickel estimated to be present. Add 20 ml in excess.

7.5.4 Make the solution slightly ammoniacal (pH of about 10) by addition of sufficient ammonium hydroxide. Stir vigorously for about 30 s and allow the precipitate to settle for 30 min.

7.5.5 Filter the solution through a medium porosity paper. Wash the precipitate five times with warm water (about 40 to 50 °C). Retain the filtrate for processing in 7.5.10.

7.5.6 Dissolve the precipitate through the filter into the beaker used for the first precipitation, using a hot mixture of 20 ml of hydrochloric acid (4.4), 10 ml of nitric acid (4.6) and 30 ml of water. Wash the filter carefully with three 20 ml portions of the acid mixture, following the addition of each portion by washing with warm water. Ensure that all the red precipitate is dissolved and finally wash the filter thoroughly with warm water.

7.5.7 Reprecipitate the nickel by repeating the steps in 7.5.2 to 7.5.4 inclusive but use only 2 ml of tartaric acid solution (4.9) and only 5 ml excess of dimethylglyoxime solution (4.3).

7.5.8 Filter the precipitate on the dried and preweighed fritted glass crucible (7.3.2). Clean the beaker thoroughly and wash the precipitate five times with warm water. Retain the filtrate for processing in 7.5.10.

7.5.9 Dry the crucible and precipitate in an oven at 150 °C for 2 h, cool in a desiccator for 60 min and weigh quickly, under the same conditions as used in 7.3.2.

2

7.5.10 Combine the filtrates from 7.5.5 and 7.5.8. Evaporate to a viscous consistency. Add 50 ml of hydrochloric acid (4.4) in 10 to 15 ml portions and heat. Add 50 ml of hot water and bring to the boil. Allow to cool and transfer to a 200 ml one-mark volumetric flask. Make up to the mark with water and mix.

7.5.11 Determine the nickel content of the combined filtrates by atomic absorption. See annex A.

NOTES

1   The nickel content of the combined filtrates should not exceed 0,2 % (m/m) nickel in the original sample.

2   High levels of nickel in the filtrates may indicate a faulty crucible.

3   If the nickel in the filtrate is high, or if the sensitivity of the atomic absorption instrument is very high, it may be necessary to dilute the solution from 7.5.10 for atomic absorption analysis.

8   Expression of results

8.1   Calculation

The nickel content, expressed as a percentage by mass, is given by the formula

$$20,32 \frac{(m_2 - m_1) \times 1\,000}{m_0 \times V} + w_f \, (\%)$$

where

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

m_1 is the mass, in grams, of the empty crucible;

m_2 is the mass, in grams, of the crucible and the nickel dimethylglyoxime precipitate;

V is the volume, in millilitres, of the aliquot part of the test solution taken in 7.5.1;

$w_f \, (\%)$ is the correction for percentage of nickel which is determined in the combined filtrates (7.5.11);

20,32 is the conversion factor, multiplied by 100, of nickel dimethylglyoxime to nickel.

8.2   Precision

8.2.1   Laboratory tests

8.2.1.1   This International Standard was subjected to an inter-laboratory test programme involving seven countries, 20 laboratories and 39 analysts. Eight samples of commercial ferro-nickel covering the range of 21 to 41 % (m/m) nickel were analysed. Each laboratory was requested to supply two determinations by each of two analysts for each sample.

8.2.1.2   The test was carried out on test solutions of 50 ml for nickel contents lower than 30 % (m/m) and 25 ml for contents higher than 30 % (m/m). These solutions became 100 ml and 50 ml, respectively, in the final procedure adopted after completion of the programme (see 7.5.1). It is expected that the repeatability and the reproducibility will be better when the method is used as specified.

8.2.2   Statistical results

Repeatability and two reproducibilities were calculated according to the principles of ISO 5725. The values resulting from this analysis are given in table 1. A report on the interlaboratory tests and statistical analysis is given in annex B.

Table 1 — Results of statistical analysis

Nickel content [% (m/m)]	15 to 30	31 to 45
Standard deviation — within analyst, s_{w1} — between analyst/within laboratory, s_{w2} — between laboratories, s_b	0,047 0,047 0,054	0,066 0,095 0,047
Repeatability, $r = 2,83 \sqrt{s_{w1}^2}$	0,13	0,19
Reproducibility, within laboratory, R_w $R_w = 2,83 \sqrt{s_{w1}^2 + s_{w2}^2}$	0,19	0,33
Reproducibility, between laboratories, R $R = 2,83 \sqrt{s_{w1}^2 + s_{w2}^2 + s_b^2}$	0,24	0,35

NOTES TO TABLE 1

1   These values of the repeatability and reproducibility can be retained as normally representative of the performance of the analytical method specified in this International Standard and applied to similar samples.

2   The repeatability and reproducibility data may be used as guidelines for establishing splitting limits.

9   Test report

The test report shall include the following information:

a)   the reference to the method used;

b)   the results of the analysis;

c)   the number of independent replications;

d)   any unusual features noted during the analysis;

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

Annex A

Determination of nickel in combined filtrates by atomic absorption spectrometry

(This annex forms an integral part of the Standard.)

A.1 General

This annex describes the procedure for the determination of residual nickel in the combined filtrates from the gravimetric determination of nickel (see 7.5.10 and 7.5.11).

A.2 Reagents

A.2.1 Hydrochloric acid, ϱ_{20} = 1,19 g/ml.

A.2.2 Nickel, standard solution, corresponding to 0,1 g of Ni per litre.

Weigh, to the nearest 0,005 g, 1,00 g of nickel metal, [99,9 % (m/m) minimum], transfer to a 600 ml beaker and dissolve in 40 ml nitric acid (ϱ_{20} = 1,41 g/ml) diluted 1 + 1. Evaporate to a viscous syrup, cool, redissolve the salts in water and transfer to a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

Pipette 25,0 ml of this solution into a 250 ml one-mark volumetric flask. Make up to the mark with water and mix.

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

A.3 Apparatus

Ordinary laboratory apparatus, and

A.3.1 Burette, of capacity 50 ml, graduated in divisions of 0,05 ml, in accordance with ISO 385/1, class A.

A.3.2 Volumetric flasks, of capacities 200; 250; and 1 000 ml, in accordance with ISO 1042, class A.

A.3.3 Pipette, of capacity 25 ml, in accordance with ISO 648, class A.

A.3.4 Atomic absorption spectrometer, equipped with a burner head for an air-acetylene flame and a nickel hollow cathode lamp.

A.4 Procedure

A.4.1 Adjustment of atomic absorption spectrometer

Set the required instrument parameters according to the manufacturer's instructions. Adjust the wavelength to 232 nm and the nickel lamp current as recommended.

Light the burner and adjust the flows of air and acetylene to obtain an oxidizing, clear, non-luminescent flame while aspirating water. Adjust the instrument to zero.

A.4.2. Preparation of the set of calibration solutions

Transfer, using a burette, 0; 2; 5; 10; and 15 ml of the nickel standard solution (A.2.2) to each of five 200 ml one-mark volumetric flasks. Add 50 ml of hydrochloric acid (A.2.1), make up to the mark with water and mix. These calibration solutions correspond to 0,0; 0,2; 0,5; 1,0; and 1,5 mg of Ni in the 200 ml volume (see 7.5.10).

A.4.3 Atomic absorption measurements

Aspirate each of the calibration solutions (A.4.2) starting with the zero member and note the absorbance reading. Flush the system by aspirating water between each reading.

Aspirate the test solution (7.5.10) and note the absorbance reading.

Repeat the measurement of calibration solutions and test solution such that the measurement of the test solution lies between the measurement of two calibration solutions.

A.4.4 Preparation of the calibration graph

Plot the instrument reading against the nickel content of the calibration solutions.

A.5 Expression of results

Using the calibration curve (A.4.4) read the amount of nickel corresponding to the measured absorbance of the test solution.

The nickel content of the filtrates, w_f (%), to be applied as a correction in 8.1, expressed as a percentage by mass of the original sample, is given by the formula

$$\frac{m_3}{m_0 \times V} \times 100$$

where

m_0 is the mass, in grams, of the test portion (7.1);

m_3 is the mass, in milligrams, of nickel in the test solution;

V is the volume, in millilitres, of the aliquot of the test solution taken in 7.5.1.

NOTES

1 For some atomic absorption instruments it may be necessary to use scale expansion.

2 It is not necessary to add dimethylglyoxime to the calibration solutions and evaporate to a viscous consistency for mineralization.

3 If the nickel content of the test solution is high then it may be diluted by a known amount and an appropriate correction made.

Annex B

Statistical report of interlaboratory tests

(This annex is given for information only.)

B.0 Introduction

This International Standard was tested in an interlaboratory programme involving seven countries, 20 laboratories and 39 analysts. Eight samples of commercial ferronickel covering the range 21 to 41 % (m/m) were analysed for nickel content. The test programme was designed to determine the repeatability and the within- and between-laboratory reproducibilities in general, in the same spirit as ISO 5725.

B.1 References

ISO 3534, *Statistics — Vocabulary and symbols.*

ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests.*

B.2 Definitions

For the purpose of this annex, the definitions of ISO 3534 apply.

Complementary information was added in the within-laboratory reproducibility which was represented by the factor of a change in analyst within a laboratory.

B.3 Design of test programme

The analytical test programme was designed with the aim of providing maximum information. Each laboratory was requested to analyse each sample in duplicate by two analysts. Thus for each participating laboratory, two pairs of results for each sample are obtained.

B.4 Test samples

This test programme used eight samples of ferronickel in the form of chips obtained by milling or drilling of ingots; in the case of milling, the chips were crushed in a vibratory crusher. These samples had nickel contents ranging from 21 to 41 % (m/m) and represented commercial qualities.

B.5 Changes in analytical procedure

The test was carried out by taking aliquots of 50 ml for contents lower than 30 % (m/m) in nickel and 25 ml for contents higher than 30 % (m/m). These aliquots have become 100 ml and 50 ml, respectively, in the final procedure adopted after completion of the test programme (see 7.5.1).

B.6 Statistical procedures

B.6.1 Statistical tests for outliers

B.6.1.1 As recommended in ISO 5725, Cochran's test was applied to compare the within-analyst fluctuations (variance of repeatability on duplicate analyses, analyst by analyst). At a probability of 95 %, this led to the rejection of four laboratories distributed among three samples.

B.6.1.2 The same test was again applied to compare the within-laboratory fluctuations at a level of analyst means. The situation is similar to the preceding one except that the "analyst level" becomes the "laboratory level" and that the "individual determination" level becomes the "analyst mean" level. At the 95 % probability level, this led to the rejection of four laboratories distributed among four samples.

B.6.1.3 For testing the comparison of means between laboratories, ISO 5725 recommends the Dixon test. This test, however, is valid only for comparison of a small number of means and it was replaced, in this analysis, by the Grubbs test which is of a more general and rigorous application for comparison of a greater number of laboratories such as, in this case, 20 laboratories. At 95 % probability, this test rejected three laboratories distributed among three samples.

B.6.2 Analysis of variance sample by sample

B.6.2.1 These were conducted in the spirit of ISO 5725 which results in a repeatability variance s_{w1}^2 and a between-laboratory variance s_b^2. But here the test design allows discrimination between the variance due to changes of analyst and another due to changes of laboratories. The statistical analysis provided the following statistical estimates:

s_{w1} is the repeatability standard deviation (within analyst);

s_{w2} is the standard deviation between analyst/within laboratory (or between analysts in the same laboratory);

s_b is the standard deviation between laboratories;

s_w is the within-laboratory reproducibility (including a change in analyst) standard deviation

$$s_w = \sqrt{s_{w1}^2 + s_{w2}^2}$$

s_R is the reproducibility standard deviation

$$s_R = \sqrt{s_{w1}^2 + s_{w2}^2 + s_b^2}$$

From this, in the spirit of ISO 5725, one can deduce:

Repeatability	$r = 2{,}83\sqrt{s_{w1}^2}$
Reproducibility, within laboratory (including a change in analyst)	$R_w = 2{,}83\sqrt{s_{w1}^2 + s_{w2}^2}$
Reproducibility, between laboratories	$R = 2{,}83\sqrt{s_{w1}^2 + s_{w2}^2 + s_b^2}$

NOTE — R_w is an intermediate quantity which is of value within a laboratory where the determinations can be made by several analysts.

B.6.2.2 Snedecor tests were applied to the variances so computed (using the F tables) which allowed testing whether, at a given probability level, the "analyst" factor or the "laboratory" factor gave any evidence of being significant. Numerical values resulting from this analysis are summarized in table 2.

B.6.3 Analysis of variance in groups of four samples

B.6.3.1 Preliminary tests have shown that the four samples of series A have a similar behaviour whereas those of series B have some different characteristics. The statistical analysis in two groups of four samples allows supplementary information to be extracted from the fact that tests of significance of variances are carried out with a greater number of degrees of freedom. A group of results is thus obtained for the lower levels and another group for the higher levels.

B.6.3.2 This more thorough analysis shows evidence, in the case of series B samples, of a sampling variance that can be extracted from the "analyst plus laboratory" variance (being $s_{w2}^2 + s_b^2$), which was not possible in sample by sample analysis. For series B, this allows slightly smaller values of s_{w2} and s_b than the simple averages of results for the four samples to be obtained. In practice, this new estimate is in better agreement with the performance of the analytical method itself. The characteristic values given in table 3 are thus obtained.

Table 2 — Analyst and laboratory factors

Sample	Nickel content [% (m/m)]	Number of analysts after rejection, n	Repeatability standard deviation, s_{w1}	Standard deviation between analyst/ within laboratory, s_{w2}	Significance of Snedecor's test in detecting analyst factor	Standard deviation between laboratories, s_b	Significance of Snedecor's test in detecting laboratory factor	Repeatability, r	Reproducibility, within laboratory, (including a change in analyst), R_w	Reproducibility, between laboratories, R
A1	21,55	34	0,065 2	0,066 4	HS[3]	0,066 1	S[2]	0,18	0,26	0,32
A2	21,76	32	0,057 0	0,079 9	THS[4]	0,026 5	NS[1]	0,16	0,28	0,29
A3	23,50	26	0,055 5	0,061 4	HS[3]	0,048 4	NS[1]	0,16	0,23	0,27
A4	25,22	38	0,056 2	0,077 5	THS[4]	0,048 7	NS[1]	0,16	0,27	0,30
B1	27,14	34	0,065 9	0,065 7	HS[3]	0,034 1	NS[1]	0,19	0,26	0,28
B2	34,90	36	0,068 6	0,145 9	THS[4]	—[5]	NS[1]	0,19	0,45	0,45
B3	37,74	36	0,087 4	0,105 6	THS[4]	0,099 1	S[2]	0,25	0,39	0,48
B4	41,11	34	0,073 8	0,093 5	THS[4]	0,124 9	HS[3]	0,21	0,34	0,49

1) NS indicates not significant at a probability of 95 %.

2) S indicates significant at a probability of 95 % but not at 99 %.

3) HS indicates highly significant at a probability of 99 % but not at 99,9 %.

4) THS indicates very highly significant at a probability of 99,9 %.

5) The numerical results obtained by conducting a conventional analysis of variance allowed estimates to be made for the two standard deviations s_{w2} and s_b except for the s_b case of the B2 sample. It is rational to regard this value as zero.

Table 3 — Results of statistical analysis by groups of four samples

Nickel content [% (m/m)]	15 to 30	31 to 45
Standard deviation		
— within analyst, s_{w1}	0,047	0,066
— between analyst/within laboratory, s_{w2}	0,047	0,095
— between laboratories, s_b	0,054	0,047
Repeatability, $r = 2,83 \sqrt{s_{w1}^2}$	0,13	0,19
Reproducibility, within laboratory, R_w $$R_w = 2,83 \sqrt{s_{w1}^2 + s_{w2}^2}$$	0,19	0,33
Reproducibility, between laboratories, R $$R = 2,83 \sqrt{s_{w1}^2 + s_{w2}^2 + s_b^2}$$	0,24	0,35