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**Methods for chemical analysis
of ferronickel**

ICS 77.100

Descriptors : ferronickel, ferro-alloys, nickel-containing alloys, chemical analysis and testing, testing

Reference number : JIS G 1326 : 2000 (E)

Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of International Trade and Industry through deliberations at the Japanese Industrial Standards Committee in accordance with the Industrial Standardization Law. Consequently **JIS G 1326 : 1987** is replaced with **JIS G 1326 : 2000**.

In this revision, in order to conform to the International Standards, Annexes 1, 3, 5, 6, 10, 11 and 12 have been adopted and this Standard expresses the determination methods for each component on the form of annex system.

JIS G 1326 has the following Annexes.

- Annex 1 (normative) *Determination of nickel content—Dimethylglyoxime gravimetric method (ISO 6352)*
- Annex 1 annex A (normative) *Determination of nickel in combined filtrates by atomic absorption spectrometric method*
- Annex 2 (normative) *Determination of nickel content—Disodium dihydrogen ethylenediamine tetraacetate titrimetric method after separation of dimethylglyoxime precipitate*
- Annex 3 (normative) *Determination of cobalt content—Flame atomic absorption spectrometric method (ISO 7520)*
- Annex 4 (normative) *Determination of carbon content—Coulometric method after combustion*
- Annex 5 (normative) *Determination of carbon content—Infra-red absorption method after combustion (ISO 7524)*
- Annex 6 (normative) *Determination of silicon content—Silicon dioxide gravimetric method (ISO 8343)*
- Annex 7 (normative) *Determination of silicon content—Molybdosilicic acid blue absorptiometric method*
- Annex 8 (normative) *Determination of manganese content—Atomic absorption spectrometric method*
- Annex 9 (normative) *Determination of phosphorus content—Molybdophosphoric acid blue absorptiometric method after extraction and separation of molybdophosphoric acid*
- Annex 10 (normative) *Determination of phosphorus content—Phosphovanadomolybdate molecular absorptiometric method (ISO 11400)*
- Annex 11 (normative) *Determination of sulfur content—Infra-red absorption method after combustion (ISO 7526)*
- Annex 12 (normative) *Determination of sulfur content—Potassium iodate titrimetric method after combustion (ISO 7527)*
- Annex 13 (normative) *Determination of sulfur content—Methylene blue absorptiometric method after vaporization and isolation of hydrogen sulfide*
- Annex 14 (normative) *Determination of chromium content—Atomic absorption spectrometric method*
- Annex 15 (normative) *Determination of copper content—Atomic absorption spectrometric method*

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Methods for chemical analysis of ferronickel

Introduction This Japanese Industrial Standard has been constructed with the Annexes 1, 3, 5, 6, 10, 11 and 12, which are specified on the basis of **ISO 6352 : 1985 Ferronickel—Determination of nickel content—Dimethylglyoxime gravimetric method**, **ISO 7520 : 1985 Ferronickel—Determination of cobalt content—Flame atomic absorption spectrometric method**, **ISO 7524 : 1985 Nickel, ferronickel and nickel alloys—Determination of carbon content—Infra-red absorption method after induction furnace combustion**, **ISO 8343 : 1985 Ferronickel—Determination of silicon content—Gravimetric method**, **ISO 11400 : 1992 Nickel, ferronickel and nickel alloys—Determination of phosphorus content—Phosphovanadomolybdate molecular absorption spectrometric method**, **ISO 7526 : 1985 Nickel, ferronickel and nickel alloys—Determination of sulfur content—Infra-red absorption method after induction furnace combustion** and **ISO 7527 : 1985 Nickel, ferronickel and nickel alloys—Determination of sulfur content—Iodimetric titration method after induction furnace combustion**), without any modification in the technical contents; and additionally with Annexes 2, 4, 7, 8, 9, 13, 14 and 15, which are the determination methods not specified in the corresponding International Standards.

1 Scope This Japanese Industrial Standard specifies the methods for determination of nickel, cobalt, carbon, silicon, manganese, phosphorus, sulfur, chromium and copper contained in ferronickel.

Remarks : The International Standards corresponding to this Standard are as follows.

- | | |
|------------------|---|
| ISO 6352 : 1985 | <i>Ferronickel—Determination of nickel content—Dimethylglyoxime gravimetric method</i> |
| ISO 7520 : 1985 | <i>Ferronickel—Determination of cobalt content—Flame atomic absorption spectrometric method</i> |
| ISO 7524 : 1985 | <i>Nickel, ferronickel and nickel alloys—Determination of carbon content—Infra-red absorption method after induction furnace combustion</i> |
| ISO 7526 : 1985 | <i>Nickel, ferronickel and nickel alloys—Determination of sulfur content—Infra-red absorption method after induction furnace combustion</i> |
| ISO 7527 : 1985 | <i>Nickel, ferronickel and nickel alloys—Determination of sulfur content—Iodimetric titration method after induction furnace combustion</i> |
| ISO 8343 : 1985 | <i>Ferronickel—Determination of silicon content—Gravimetric method</i> |
| ISO 11400 : 1992 | <i>Nickel, ferronickel and nickel alloys—Determination of phosphorus content—Phosphovanadomolybdate molecular absorption spectrometric method</i> |

2 Normative references The following standards contain provisions which, through reference in this Standard, constitute provisions of this Standard. The most recent editions of the standards indicated below shall be applied.

JIS G 1301 *General rules for chemical analysis of ferroalloys*

JIS K 8001 *General rule for test methods of reagents*

JIS K 8005 *Reference materials for volumetric analysis*

JIS Z 2615 *General rules for determination of carbon in metallic materials*

JIS Z 2616 *General rules for determination of sulfur in metallic materials*

3 General General matters common to the operations for the determination shall be in accordance with **JIS G 1301**. Provided that this shall not apply to the Annexes 1, 3, 5, 6, 10, 11 and 12.

4 Classification of determination methods The determination methods for chemical components in ferronickel shall be classified as shown in Table 1.

Table 1 Determination methods for components in ferronickel

Component	Determination method	Applicable limit of content % (m/m)	No. of Annex (normative)
Nickel	• Dimethylglyoxime gravimetric method (ISO 6352)	15 or over up to and incl. 60	1
	• Disodium dihydrogen ethylenediamine tetraacetate titrimetric method after separation of dimethylglyoxime precipitate	15 or over up to and incl. 60	2
Cobalt	• Flame atomic absorption spectrometric method (ISO 7520)	0.025 or over up to and incl. 2.5	3
Carbon	• Coulometric method after combustion	0.001 or over up to and incl. 3	4
	• Infra-red absorption method after combustion (ISO 7524)	0.001 or over up to and incl. 2	5
Silicon	• Silicon dioxide gravimetric method (ISO 8343)	0.2 or over up to and incl. 4	6
	• Molybdosilicic acid blue absorptiometric method	0.01 or over up to and incl. 0.5	7
Manganese	• Atomic absorption spectrometric method	0.01 or over up to and incl. 0.5	8
Phosphorus	• Molybdophosphoric acid blue absorptiometric method after extraction and separation of molybdophosphoric acid	0.001 or over up to and incl. 0.03	9
	• Phosphovanadomolybdate molecular absorptiometric method (ISO 11400)	0.000 5 or over up to and incl. 0.05	10
Sulfur	• Infra-red absorption method after combustion (ISO 7526)	0.001 or over up to and incl. 0.3	11
	• Potassium iodate titrimetric method after combustion (ISO 7527)	0.001 or over up to and incl. 0.3	12
	• Methylene blue absorptiometric method after vaporization and isolation of hydrogen sulfide	0.001 or over up to and incl. 0.05	13
Chromium	• Atomic absorption spectrometric method	0.01 or over up to and incl. 3	14
Copper	• Atomic absorption spectrometric method	0.01 or over up to and incl. 0.2	15

Annex 1 (normative)
Determination of nickel content—
Dimethylglyoxime gravimetric method

Introduction This Annex 1 has been prepared based on the first edition of **ISO 6352 Ferronickel—Determination of nickel content—Dimethylglyoxime gravimetric method** published in 1985, without modifying the technical contents.

The portions underlined with dots in this Annex show the matters not specified in the original International Standard.

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

2 Normative references

JIS R 3505 *Volumetric glassware*

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*

Informative reference : **ISO 5725** is replaced with the following standards.

ISO 5725-1 to 6 : 1994 *Accuracy (trueness and precision)*
of measurement methods and results—Part 1 to 6

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 $\rho_{20} = 1.05 \text{ g/ml}$, diluted (1+1)

4.2 Aqueous ammonia $\rho_{20} = 0.925 \text{ g/ml}$

4.3 Dimethylglyoxime 10 g/ml solution in ethanol

4.4 Hydrochloric acid $\rho_{20} = 1.19 \text{ g/ml}$

4.5 Hydrochloric acid $\rho_{20} = 1.19 \text{ g/ml}$, diluted (1+9)

4.6 Nitric acid $\rho_{20} = 1.41 \text{ g/ml}$

4.7 Nitric acid $\rho_{20} = 1.41 \text{ g/ml}$, diluted (1+1)

4.8 Perchloric acid $\rho_{20} = 1.61 \text{ g/ml}$ [72 % (m/m)]

4.9 Tartaric acid 500 g/l solution

4.10 Hydrofluoric acid $\rho_{20} = 1.14 \text{ g/ml}$, 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 Apparatus shall be the ordinary laboratory apparatus and be the following.

5.1 Glass filter Made of fritted glass, of approximately 10 to 20 μm pore diameter.

5.2 Glass beaker Of capacity 600 ml, clean, unetched and flat bottomed.

5.3 Pipette Of capacities 50 and 100 ml, in accordance with JIS R 3505 Class A or ISO 648 Class A.

5.4 Volumetric flask Of capacities 200 and 1 000 ml, in accordance with JIS R 3505 Class A or 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 relevant International Standard.

6.2 The laboratory samples normally is in the form of a powder, 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 sample should be obtained by riffing.

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 draft chamber 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 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 glass filter

7.3.1 Filter through the glass filter (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 glass filter with warm water until all the acid has been removed.

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

- Remarks 1 This procedure is used to condition a new glass filter or to clean a used glass filter after the analysis is completed.
- 2 For highest accuracy, the glass filter and precipitate (7.5.9) should be weighed, as closely as possible, under the same temperature and humidity conditions as the empty glass filter.

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 (1+1). Cover the beaker with a watch glass and heat gently, if necessary to complete dissolution.

Remarks : For ferronickel samples containing more than 1 % (m/m) silicon, use a polytetrafluoroethylene beaker (5.5). Attack the sample 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 the fumes of per perchloric acid emits. 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. Cover the beaker with a watch glass, reflux at this temperature for 20 min and proceed as directed in 7.4.2, "Remove the beaker from the hotplate and allow to cool ...".

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. Cover the beaker with a watch glass, 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 silicon dioxide using a medium porosity filter paper (5 grade B), collecting the filtrate in a 1 000 ml volumetric flask. Rinse the beaker and wash the silicon dioxide precipitate three times with hydrochloric acid (4.5) and then four times with warm water. Discard the silicon dioxide precipitate, and make up the filtrate to the mark with water.

7.5 Determination

7.5.1 Pipette from the test solution into a 600 ml beaker (5.2), an aliquot containing 60 to 120 mg of nickel, and dilute to 300 ml with water. To make the aliquot containing 60 to 120 mg of nickel, 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 this solution (7.5.1). Pour in, while stirring, aqueous ammonia (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. Add 20 ml in excess.

7.5.4 Make the solution slightly ammoniacal (pH of about 10) by addition of sufficient aqueous ammonia (4.2). 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 filter paper (5 grade B). 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 of 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 paper thoroughly with warm water.

7.5.7 Reprecipitate the nickel by repeating the steps in 7.5.2 to 7.5.4. However, 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 precipitation on the dried and preweighed fritted glass filter (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 glass filter and precipitate in a drying oven at 150 °C for 2 h, cool in a desiccator for 60 min and weigh quickly, under the same temperature and humidity as used in 7.3.2.

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 volumetric flask. Make up to the mark with water.

7.5.11 Determine the nickel content of the combined filtrates by atomic absorption spectrometric method. See Annex 1 Annex A.

Remarks 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 glass filter.
- 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 following formula.

$$Ni = 20.32 \times \frac{(m_2 - m_1) \times 1\,000}{m_0 \times V} + W_f$$

where, Ni : the content of nickel [% (m/m)]
 m_0 : the mass of the test portion (g)
 m_1 : the mass of the empty glass filter (g)
 m_2 : the mass of the glass filter and nickel dimethylglyoxime precipitate (g)
 V : the volume of the aliquot of the test solution taken in 7.5.1 (ml)
 W_f : the mass percentage of nickel in the sample which is converted from the nickel percentage in the combined filtrates (7.5.11) [% (m/m)]
20.32 : the conversion factor, multiplied by 100, of nickel dimethylglyoxime to nickel

8.2 Precision

8.2.1 Laboratory tests

8.2.1.1 The method specified in this Annex was subjected to an interlaboratory test programme involving seven countries, 20 laboratories and 39 analysts. Eight samples of commercial ferronickel covering the range of 21 to 41 % (m/m) nickel content 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 solution of 50 ml for nickel contents lower than 30 % (m/m) and 25 ml for contents higher than 30 % (m/m). These solution 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 amount of aliquot increases.

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 Annex 1 Table 1. A detail on the interlaboratory tests and statistical analysis is given in Annex 1 Informative reference B.

Annex 1 Table 1 Results of statistical analysis

Statistical items	Nickel content % (m/m)	
	15 to 30	31 to 45
Standard deviation—within analyst, S_{w1}	0.047	0.066
Standard deviation—between analyst/within laboratory, S_{w2}	0.047	0.095
Standard deviation—between laboratories, S_b	0.054	0.047
Repeatability, $r = 2.83 \sqrt{S_{w1}^2}$	0.13	0.19
Reproducibility, within laboratory, $R_w = 2.83 \sqrt{S_{w1}^2 + S_{w2}^2}$	0.19	0.33
Reproducibility, between laboratories, $R = 2.83 \sqrt{S_{w1}^2 + S_{w2}^2 + S_b^2}$	0.24	0.35

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

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

Informative reference : The splitting limits mean the allowable difference of analysis values between supplier side and purchaser side, and usually it is fixed up on the sales contract.

9 Test report The test report shall include the following information:

- the normative references to the method used;
- the results of the analysis;
- the number of independent replications;
- any unusual features noted during the analysis;
- any operation not included in this Annex or regarded as optional.

Annex 1 Annex A (normative)
Determination of nickel in combined filtrates
by atomic absorption spectrometric method

This Annex A forms an integral part of the Annex 1.

A.1 General This Annex A describes the procedure for the determination of residual nickel in the combined filtrates obtained when the gravimetric determination of nickel is carried out (see 7.5.10 and 7.5.11).

A.2 Reagents

A.2.1 Hydrochloric acid, $\rho_{20} = 1.19 \text{ g/ml}$

A.2.2 Nickel standard solution Corresponding to 0.1 gNi/l.

Weigh, to the nearest 0.005 g, 1.00 g of nickel metal [99.9 % (m/m) minimum], transfer into a beaker (600 ml), and dissolve in 40 ml nitric acid ($\rho_{20} = 1.41 \text{ g/ml}$) (1+1). Evaporate to a viscous syrup, cool, redissolve the salts in water and transfer to a 1 000 ml volumetric flask. Make up to the mark with water.

Pipette 25.0 ml of this solution into a 250 ml volumetric flask. Make up to the mark with water.

1 ml of this standard solution contains 0.1 mg of Ni.

A.3 Apparatus Apparatus shall be the ordinary laboratory apparatus and be the following.

A.3.1 Burette Of capacity 50 ml, graduated in divisions of 0.05 ml, in accordance with JIS R 3505 Class A or ISO 385-1 Class A.

A.3.2 Volumetric flask Of capacities 200, 250 and 1 000 ml, in accordance with JIS R 3505 Class A or ISO 1042 Class A.

A.3.3 Pipette Of capacity 25 ml, in accordance with JIS R 3505 Class A or ISO 648 Class A.

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

A.4 Procedure

A.4.1 Adjustment of atomic absorption spectrometer Set 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 ml, 2 ml, 5 ml, 10 ml and 15 ml of the nickel standard solution (A.2.2) to each of five 200 ml volumetric flasks. Add 50 ml of hydrochloric acid (A.2.1), and make up to the mark with water. These calibration solutions correspond to 0.0 mg, 0.2 mg, 0.5 mg, 1.0 mg 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 of combined filtrate (7.5.10) and note the absorbance reading.

Repeat the measurement of calibration solutions and the filtrate 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 filtrate.

The nickel content of the filtrates, W_f [% (m/m)], to be applied as a correction in 8.1, expressed as a percentage by mass of the original sample, is given by the following formula.

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

where, m_0 : the mass of the sample (g)

m_3 : the mass of nickel detected in combined filtrate (mg)

V : the volume of the aliquot of the test solution taken in 7.5.1 (ml)

- Remarks
- 1 For some atomic absorption instruments it may be necessary to use scale expansion.
 - 2 When preparing a calibration solution, it is not necessary to add dimethylglyoxime solutions and evaporate to a viscous consistency.
 - 3 If the nickel content of the filtrate is high, it is needed to dilute to make suitable concentration.

Annex 1 Informative reference B

Statistical report of interlaboratory tests

This Informative reference B gives information only, and does not form part of Annex 1.

B.0 Introduction The method specified in this Annex was tested in an inter-laboratory 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 Normative references

ISO 3534 *Statistics—Vocabulary and symbols*

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

Informative reference : **ISO 5725** is replaced with the following standards.

ISO 5725-1 to 6 : 1994 Accuracy (trueness and precision) of measurement methods and results—Part 1 to 6

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. 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 $R = 2.83 \sqrt{S_{w1}^2 + S_{w2}^2 + S_b^2}$

Remarks : 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 Annex 1 Table 2.

B.6.3 Analysis of variance in two 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 Annex 1 Table 3 are thus obtained.

Annex 1 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.

Annex 1 Table 3 Results of statistical analysis

Statistical items	Nickel content % (m/m)	
	15 to 30	31 to 45
Standard deviation—within analyst, S_{w1}	0.047	0.066
Standard deviation—between analyst/within laboratory, S_{w2}	0.047	0.095
Standard deviation—between laboratories, S_b	0.054	0.047
Repeatability, $r = 2.83 \sqrt{S_{w1}^2}$	0.13	0.19
Reproducibility, within laboratory, $R_w = 2.83 \sqrt{S_{w1}^2 + S_{w2}^2}$	0.19	0.33
Reproducibility, between laboratories, $R = 2.83 \sqrt{S_{w1}^2 + S_{w2}^2 + S_b^2}$	0.24	0.35

Annex 2 (normative)

Determination of nickel content— Disodium dihydrogen ethylenediamine tetraacetate titrimetric method after separation of dimethylglyoxime precipitate

1 Summary Decompose the sample with nitric acid, add perchloric acid, heat to evolve white fumes of perchloric acid, and then dissolve salts with hydrochloric acid. Add tartaric acid and aqueous ammonia to make the solution weak alkaline, add dimethylglyoxime to make precipitate of nickel, filter, and dissolve the precipitate with nitric acid. Then, add tartaric acid, make the solution weak alkaline with aqueous ammonia, then carry out any of the following procedures; titrate it with disodium dihydrogen ethylenediamine tetraacetate (hereafter referred to as “EDTA”) standard solution using indicator of murexide, or add ammonium acetate to make the solution weak acidic, and titrate it with EDTA standard solution using indicator of Cu-PAN, or add definite amount of EDTA standard solution, adjust its acid concentration with aqueous ammonia and nitric acid, add acetic acid and ammonium acetate to make it weak acidic, and back-titrate superfluously added EDTA with zinc standard solution using indicator of xylenol orange. The residual nickel, which will be found in the filtrate after filtration of precipitate and washings, shall be determined by means of atomic absorption spectrometric method, and the result shall be corrected.

2 Reagents Reagents shall be as follows.

- a) **Hydrochloric acid**
- b) **Hydrochloric acid (1+1, 1+9)**
- c) **Nitric acid (1+1)**
- d) **Perchloric acid**
- e) **Hydrofluoric acid**
- f) **Sulfuric acid (1+1)**
- g) **Aqueous ammonia**
- h) **Aqueous ammonia (1+1)**
- i) **Sodium disulfate**
- j) **Washing solution** Add one drop of aqueous ammonia in about 500 ml warm water, and mix well. Prepare a fresh solution at each use.
- k) **Tartaric acid solution (200 g/l)**
- l) **Ammonium acetate solution (500 g/l)**
- m) **Acetic acid-ammonium acetate solution** Dissolve 250 g of ammonium acetate in water, dilute it with water up to 1 000 ml and add 25 ml of acetic acid.
- n) **Dimethylglyoxime solution** Dissolve 1 g of dimethylglyoxime in 100 ml of ethanol (95).

- o) **0.02 mol/l EDTA standard solution** Dissolve 7.5 g of EDTA dihydrate in about 100 ml of water, transfer it into a 1 000 ml volumetric flask with rinsing the beaker with water and dilute up to the mark. Nickel quantity equivalent to 1 ml of this solution shall be obtained by either of the following procedures.

1) Case of using murexide as indicator

- 1.1) Weigh 0.600 0 g of nickel (99.9 % minimum), place it into a beaker (300 ml), cover it with a watch glass, add 30 ml of nitric acid (1+1), heat it gently to dissolve, allow it to cool to ordinary temperature, transfer, into a 1 000 ml volumetric flask with rinsing the beaker with water, and add water up to the mark to prepare nickel standard solution (600 µgNi/ml). Take a 50 ml aliquot of this nickel standard solution into a beaker (300 ml).
- 1.2) Carry out the procedure as shown in 4.3 a) 2), and calculate the nickel quantity equivalent to 1 ml of 0.002 mol/l EDTA standard solution according to the following formula.

$$f = \frac{50}{1\,000} \times \frac{G}{V}$$

where, f : the mass of nickel equivalent to 1 ml of 0.02 mol/l EDTA standard solution (g)

G : the mass of nickel weighed at 1.1) (g)

V : the consumed volume of 0.02 mol/l EDTA standard solution (ml)

2) Case of using Cu-Pan as indicator

- 2.1) After carrying out the procedure as shown in 1) 1.1), add water to make a total 150 ml.
- 2.2) Carry out the procedure in 4.3 b) 2), and calculate the nickel quantity equivalent to 1 ml of 0.002 mol/l EDTA standard solution according to the following formula.

$$f = \frac{50}{1\,000} \times \frac{G}{V}$$

where, f : the mass of nickel equivalent to 1 ml of 0.02 mol/l EDTA standard solution (g)

G : the mass of nickel weighed at 2.1) (g)

V : the consumed volume of 0.02 mol/l EDTA standard solution (ml)

3) Case of using xylenol orange as indicator

- 3.1) Carry out the procedure as shown in 1) 1.1).
- 3.2) Carry out the procedure in 4.3 c) 2), and calculate the nickel quantity equivalent to 1 ml of 0.002 mol/l EDTA standard solution according to the following formula.

$$f = \frac{50}{1000} \times \frac{G}{V_1 - V_2 \times F}$$

- where, f : the mass of nickel equivalent to 1 ml of 0.02 mol/l EDTA standard solution (g)
 G : the mass of nickel weighed at 3.1) (g)
 V_1 : the consumed volume of 0.02 mol/l EDTA standard solution (ml)
 V_2 : the consumed volume of 0.02 mol/l zinc standard solution (ml)
 F : the factor of 0.02 mol/l zinc standard solution to 0.02 mol/l EDTA standard solution

- p) **0.02 mol/l zinc standard solution** Weigh 1.30 g of zinc (99.9 % minimum), place it into a beaker (500 ml), cover the beaker with a watch glass, add 20 ml of hydrochloric acid (1+1), and heat it gently to dissolve. Allow it to cool to ordinary temperature, and add water to make a total of 1 000 ml. The standardization of this solution shall be carried out as follows.

Take accurately a 25 ml aliquot from 0.02 mol/l EDTA standard solution [o] into a beaker (300 ml), add water to make a total of about 150 ml, pour 3 to 5 drops of xylenol orange solution as indicator, add 25 ml of acetic acid-ammonium acetate solution [m]), and allow it to stand for about 10 min. Titrate this solution with 0.02 mol/l zinc standard solution, make it an end point when the solution turns reddish violet from yellow, find the consumed quantity of 0.02 mol/l zinc standard solution, and calculate the factor of 0.02 mol/l zinc standard solution to 0.02 mol/l EDTA standard solution according to the following formula.

$$F = \frac{25}{V}$$

- where, F : the factor of 0.02 mol/l zinc standard solution to 0.02 mol/l EDTA standard solution
 V : the consumed volume of 0.02 mol/l zinc standard solution (ml)

- q) **Nickel standard reference solution (100 µgNi/ml)** Weigh 1.000 g of nickel (99.5 % minimum), place it into a beaker (300 ml), cover it with a watch glass, add 30 ml of nitric acid, heat it gently to decompose the nickel. Allow it to cool to ordinary temperature, wash the lower surface of the watch glass with water, remove it, transfer the solution into a 1 000 ml volumetric flask with rinsing the beaker with water, add water up to the mark, and make this solution as a stock solution (1 mgNi/ml). Dilute accurately ten times the required amount of this stock solution with water each time the nickel standard solution is needed.
- r) **Bromothymol blue solution (1 g/l)** Preparation method shall follow 4.4 of JIS K 8001.
- s) **Murexide dilution powder** Mix 0.5 g of murexide and 50 g of dried sodium chloride, and grind them in a mortar to make them uniform.
- t) **Cu-PAN solution** Dissolve 1 g of Cu-PAN [mixture of Cu-EDTA and 1-(2-pyridylazo)-2-naphthol] in 100 ml of 2-propanol (50 v/v%).

u) **Xylenol orange solution (1 g/l)**

3 Test portion Weigh the sample, to the nearest 0.1 mg, as shown in Annex 2 Table 1 depending on the nickel content⁽¹⁾.

Annex 2 Table 1

Nickel content in sample % (m/m)	Test portion g
15 or over to and excl. 30	0.80 to 2.0
30 or over up to and incl. 60	0.40 to 1.0

Note ⁽¹⁾ When weighing the sample, it is necessary not only to follow Annex 2 Table 1 but also to make the quantity of nickel be 200 to 300 mg.

4 Procedure

4.1 Decomposition of sample The decomposition of sample shall be carried out as specified in the following procedures.

- Weigh the sample into a beaker (300 ml), cover the beaker with a watch glass, add 30 ml of nitric acid (1+1), and heat it gently to decompose the sample. Add 30 ml of perchloric acid, heat to evaporate until the vapor of perchloric acid refluxes on the inside wall of the beaker, and successively heat on for about 20 min to make thorough decomposition.
- After allowing it to cool, add 20 ml of hydrochloric acid (1+1) and 50 ml of warm water, and heat it to dissolve soluble salts. Wash the lower surface of the watch glass with water, remove the watch glass, filter the solution through a filter paper (5 grade B), wash 3 or 4 times with hydrochloric acid (1+9) that has been heated at 40 to 60 °C, and then wash sufficiently with warm water⁽²⁾. Cool the filtrate and washings to ordinary temperature, transfer them into a 500 ml volumetric flask with rinsing the beaker with water, and dilute with water up to the mark.

Note ⁽²⁾ If there is an apprehension that the residue contains nickel, the following procedures are necessary; transfer the residue into a platinum crucible (No. 30) together with filter paper, and after drying it, heat it gently until it is ashed. After allowing it to cool, moist it with 2 to 3 drops of sulfuric acid (1+1), add 3 to 5 ml of hydrofluoric acid, and heat to evaporate silicon dioxide and sulfuric acid with care not to scatter splash. After allowing it to cool, add 2 to 3 g of sodium bisulfate, and heat it gently to fuse. After allowing to cool again, dissolve the fused with a little warm water and about 1 ml of hydrochloric acid, and put this solution together with the filtrate and washings.

4.2 Formation and separation of precipitate The formation and separation of precipitate shall be carried out as specified in the following procedure.

- Take 50 ml of an aliquot from the solution obtained at 4.1 b) into a beaker (500 ml), add 25 ml of tartaric acid solution, and add water to make a total of about 300 ml.

- b) Into this solution, add 2 or 3 drops of bromothymol blue solution [2 r)] as indicator, add aqueous ammonia, while stirring, until the solution turns green from yellow, and then add about 5 ml⁽³⁾ in excess. Heat the solution up to about 70 °C, add dimethylglyoxime solution [2 n)], while stirring, at the rate of 4 ml of dimethylglyoxime solution to 10 mg of nickel plus cobalt in the solution, and then add 20 ml in excess. Stir vigorously the solution for about 30 s, heat it on to keep the solution at a temperature of about 70 °C for about 10 min, then allow to stand at room temperature for about 2 h⁽⁴⁾, and mature the precipitate of dimethylglyoxime.
- c) Filter the precipitate through a filter paper (5 grade A), and wash well it with washing solution [2 j)]. Retain the filtrate and washing solution⁽⁵⁾.
- d) Transfer the precipitate on the filter paper into the original beaker with rinsing the filter paper with warm water. Drop 20 ml of nitric acid (1+1) warmed at 40 to 60 °C onto the filter paper to dissolve the precipitate remaining on the filter paper, and wash well the filter paper with warm water. Put filtrate and washings into the original beaker, boil it for 4 to 5 min, and decompose the dimethylglyoxime.

Notes ⁽³⁾ This solution must be transparent. And, the pH at this point shall be about 9.5.

⁽⁴⁾ Alternatively, it is passable to mature the precipitate by cooling with water for about 30 min.

⁽⁵⁾ The nickel remaining in the filtrate and washings is determined by the procedure in 4.4, and retain it to correct the results.

4.3 Titration Titration shall be carried out by either of the following procedures.

a) Case of using murexide as indicator

- 1) Heat the solution obtained at 4.2 d) to evaporate until it becomes 2 to 3 ml. After allowing to cool, add about 30 ml of water.
- 2) Add 1 ml of tartaric acid [2 k)], drop aqueous ammonia (1+1), while stirring, until the solution turns bluish green from green, add 10 ml in excess, and add water to make a total about 100 ml⁽⁶⁾. Allow this solution to cool to ordinary temperature, add about 0.1 g of murexide dilution powder [2 s)] as indicator, titrate it with 0.02 mol/l EDTA standard solution [2 o)], make it an end point when the solution turns purple from yellow, and find the consumed amount of 0.02 mol/l EDTA standard solution.

b) Case of using Cu-PAN as indicator

- 1) Add water in the solution obtained at 4.2 d) to make total about 150 ml.
- 2) Into this solution add 5 drops of Cu-PAN solution [2 t)] as indicator, add little by little, while stirring, ammonium acetate solution [2 l)], and when the solution turns reddish purple from yellow, add 10 ml⁽⁷⁾ in excess. Heat this solution just before boiling, immediately titrate it with 0.02 mol/l EDTA standard solution [2 o)], make it an end point when the solution turns yellow from reddish purple, and find the consumed amount of 0.02 mol/l EDTA standard solution.

c) Case of using xylenol orange as indicator

- 1) Allow the solution obtained at **4.2 d)** to cool.
- 2) Add 0.02 mol/l EDTA standard solution [**2 o)**] at the rate of 10 ml of this standard solution to the anticipated 10 mg of the nickel in the solution, then add accurately 3 to 5 ml in excess, add 3 to 5 drops of xylenol orange solution as indicator. While stirring, drop aqueous ammonia (1+1) until the solution turns to reddish purple from yellow, and add water to make a total about 150 ml. While stirring the solution, drop nitric acid (1+1) until the solution turns yellow from reddish purple, add 25 ml of acetic acid-ammonium acetate solution [**2 m)**]⁽⁸⁾, and then allow it to stand for about 10 min. Titrate this solution with 0.02 mol/l zinc standard solution [**2 p)**], make it an end point when the solution turns reddish purple from yellow, and find the consumed amount of 0.02 mol/l zinc standard solution.

Notes ⁽⁶⁾ The value of pH at this point is about 10.

⁽⁷⁾ The value of pH at this point is about 4.0 to 4.3.

⁽⁸⁾ The value of pH at this point is about 5.5 to 5.7.

4.4 Determination of nickel in filtrate and washings The determination of nickel in the filtrate and washings shall be carried out as specified in the following procedure.

- a) Put the filtrate and washings retained at **4.2 c)** in a beaker (500 ml), heat it to evaporate until the solution becomes about 50 ml, and add 25 ml of hydrochloric acid. Allow it to cool to ordinary temperature, transfer the solution into a 100 ml volumetric flask with rinsing the beaker with water, and dilute up to the mark with water.
- b) Spray a portion of the solution in the acetylene-air flame of the atomic absorption spectrometer which has been zero-adjusted with water, and measure its absorbance at 232.0 nm wavelength.
- c) Prepare several 100 ml volumetric flasks, add stepwise from 0 to 10.0 ml (from 0 to 1 mg of nickel) of nickel standard solution [**2 q)**], add respectively 25 ml of hydrochloric acid, and add water up to the mark. Thereafter, carry out the procedures in **b)** in parallel with the procedure for filtrate and washings, and draw the relation curve between obtained values of absorbance and quantities of nickel. Thus the calibration graph is obtained.
- d) Making use of the absorbance obtained at **b)** and the calibration graph drawn at **c)**, find the quantity of nickel, and make it the nickel quantity that has remained in the filtrate and washings.

5 Calculation The nickel content in the sample shall be calculated as specified in the following formula.

5.1 Case of using murexide or Cu-PAN as indicator

$$Ni = \frac{V \times f + m_1}{m \times \frac{50}{500}} \times 100$$

where, Ni : the nickel content in the sample [% (m/m)]
 V : the consumed volume, obtained at a) 2) or b) 2) in 4.3, of 0.02 mol/l EDTA standard solution (ml)
 f : the mass of nickel equivalent to 1 ml of 0.02 mol/l EDTA standard solution (g)
 m_1 : the mass of nickel remaining in the filtrate and washings obtained at 4.4 d) (g)
 m : the mass of the test portion (g)

5.2 Case of using xylenol orange as indicator

$$Ni = \frac{(V_1 - V_2 \times F) \times f + m_1}{m \times \frac{50}{500}} \times 100$$

where, Ni : the nickel content in the sample [% (m/m)]
 V_1 : the consumed volume, obtained at 4.3 c) 2), of 0.02 mol/l EDTA standard solution (ml)
 V_2 : the consumed volume, obtained at 4.3 c) 2), of 0.02 mol/l zinc standard solution (ml)
 F : the factor of 0.02 mol/l zinc standard solution to 0.02 mol/l EDTA standard solution
 f : the mass of nickel equivalent to 1 ml of 0.02 mol/l EDTA standard solution (g)
 m_1 : the mass of nickel remaining in the filtrate and washings obtained at 4.4 d) (g)
 m : the mass of the test portion (g)

6 Precision of determination The precision of determination for this method shall be as shown in Annex 2 Table 2.

Annex 2 Table 2

Unit : % (m/m)

Nickel content in sample	Standard deviation within laboratory ⁽⁹⁾	Standard deviation between laboratories ⁽¹⁰⁾
15 or over to and excl. 30	0.045	0.065
30 or over up to and incl. 60	0.065	0.105

Notes ⁽⁹⁾ The standard deviation within laboratory shows the precision given when determination is carried out repeatedly in the same laboratory.

⁽¹⁰⁾ The standard deviation between laboratories shows the precision between averages of two laboratories when two determinations are carried out repeatedly in each laboratory.

Annex 3 (normative)
Determination of cobalt content—
Flame atomic absorption spectrometric method

Introduction This Annex 3 is has been prepared based on the first edition of **ISO 7520 Ferronickel—Determination of cobalt content—Flame atomic absorption spectrometric method**, published in 1985, without modifying the technical content.

The portions underlined with dots in this Annex show the matters not specified in the original International Standard.

1 Scope This Annex 3 specifies a flame atomic absorption spectrometric method for the determination of the cobalt content in ferronickel.

This method is applicable to the ferronickel whose cobalt content is in the range 0.025 to 2.5 %(*m/m*).

2 Normative references

JIS R 3505 Volumetric glassware

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

ISO 6352 Ferronickel—Determination of nickel content—Dimethylglyoxime gravimetric method

Informative reference : ISO 5725 is replaced with the following standards.

ISO 5725-1 to 6 : 1994 Accuracy (trueness and precision) of measurement methods and results—Part 1 to 6

3 Principle Dissolve a sample in acid mixture of nitric acid and hydrochloric acid, treat it with perchloric acid to precipitate silicon dioxide, filter it for elimination of silicon dioxide. Add lanthanum solution, for elimination of potential interference, spray it in a acetylene-air flame of atomic absorption spectrometric apparatus, and measure the absorbance at the wavelength of 240.7 nm for the determination of cobalt.

Remarks : This analysis can be carried out on the solutions which have been prepared for the determination of nickel by **ISO 6352**.

When the laboratory data has small dispersion, cobalt can be determined by using of the sample solution prepared in Annex 8, Annex 14 and Annex 15.

4 Reagents Unless otherwise specified, during the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Hydrochloric acid $\rho_{20} = 1.19 \text{ g/ml}$

4.2 Hydrochloric acid $\rho_{20} = 1.19 \text{ g/ml}$, diluted (1+9)

4.3 Nitric acid $\rho_{20} = 1.41 \text{ g/ml}$, diluted (1+1)

4.4 Perchloric acid $\rho_{20} = 1.61 \text{ g/ml}$, [72 % (m/m)]

4.5 Hydrofluoric acid $\rho_{20} = 1.14 \text{ g/ml}$, 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.

4.6 Lanthanum solution 200 gLa/l Weigh 250 g of lanthanum chloride hexahydrate ($\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$) into a beaker (600 ml). Add 25 ml of hydrochloric acid (4.1) and 300 ml of water. Stir to complete dissolution. If necessary, filter, into a 500 ml volumetric flask, make up to the mark with water and mix.

4.7 Nickel plus iron matrix solution (12 gNi + 28 gFe)/l

4.7.1 Weigh 12.0 g of high purity nickel powder [containing less than 0.001 % (m/m) cobalt] into a beaker (800 ml), and add 50 ml of water and 50 ml of nitric acid ($\rho_{20} = 1.41 \text{ g/ml}$). When the first reaction is finished, stir and heat to complete decomposition. Add water to make total about 250 ml.

4.7.2 Weigh 28.0 g of high purity iron powder [containing less than 0.001 % (m/m) cobalt] into a beaker (800 ml), and add 100 ml of hydrochloric acid (1+1). Carefully add 50 ml of nitric acid ($\rho_{20} = 1.41 \text{ g/ml}$), and heat to complete dissolution and oxidation of iron. Dilute to about 250 ml with water.

4.7.3 Carefully combine the nickel solution (4.7.1) with the iron solution (4.7.2). Filter into a 1 000 ml volumetric flask, and make up to the mark with water.

4.8 Cobalt standard solution (0.500 gCo/l) Weigh, to the nearest 0.001 g, 0.500 g of high purity [99.9 % (m/m) minimum] cobalt powder, transfer to a beaker (600 ml), and add 40 ml of nitric acid (4.3). Heat to complete dissolution, boil gently to expel oxides of nitrogen, cool and transfer to a 1 000 ml volumetric flask containing 160 ml of nitric acid (4.3). Make up to the mark with water.

1 ml of this standard solution contains 0.500 mg of Co.

5 Apparatus Apparatus shall be of the ordinary laboratory apparatus and the following.

5.1 Atomic absorption spectrometer Equipped with a laminar flow burner for an air-acetylene flame and a cobalt hollow cathode lamp.

5.2 Burette Of capacity 50 ml, graduated in divisions of 0.1 ml, in accordance with JIS R 3505, class A or ISO 385-1, class A.

5.3 Glass beakers Of capacity 600 ml, clean, unetched and flat bottomed.

5.4 Pipette Of capacity 25 and 50 ml, in accordance with JIS R 3505, class A or ISO 648, class A.

5.5 Volumetric flasks Of capacities 250, 500 and 1 000 ml in accordance with JIS R 3505, class A or ISO 1042, class A.

5.6 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 samples shall be carried out by normal agreed procedures or, in case of dispute, by the relevant International Standard.

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

6.3 If it is suspected that the laboratory samples 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 or 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 a fume draft chamber 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 glass beaker (5.3).

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 test solution

7.3.1 Dissolve the test portion (7.1) by adding 25 ml of water followed by 50 ml of nitric acid (4.3). 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 (5.6). Attack the sample by adding successively 25 ml of water, 40 ml of nitric acid (4.3) and 10 ml of hydrochloric acid (4.1). To obtain complete dissolution of the sample, add, at the end of effervescence, 10 ml of hydrofluoric acid (4.5) and 40 ml of perchloric acid (4.4). Heat until evolution of fumes of perchloric acid. Allow to cool and transfer the solution quantitatively to a glass beaker (5.3). Heat at 260 °C until abundant white fumes are obtained.

Cover the beaker with a watch glass. Reflux at this temperature for 20 min and proceed as directed in 7.3.2 "Remove the beaker from the hotplate and allow to cool." and downward.

7.3.2 When the metal is dissolved, add 40 ml of perchloric acid (4.4) and heat at 260 °C until abundant white fumes are obtained. Cover the beaker with a watch glass and reflux at this temperature for 20 min. Remove the beaker from the hotplate and allow to cool. Add 20 ml of hydrochloric acid (4.1) and 200 ml of warm water. Filter off the silicon dioxide using a medium porosity filter paper (5 grade B), collecting the filtrate in a 1 000 ml volumetric flask. Rinse the beaker and wash the silicon dioxide precipitate three times with hydrochloric acid (4.2) and four times with warm water. Discard the silicon dioxide precipitate. Add 50 ml of lanthanum solution (4.6) to the filtrate, and add water to make up to the mark (test solution A).

7.4 Preparation of calibration solutions

7.4.1 Set A for calibration solution

7.4.1.1 Transfer six 50.0 ml volumes of the nickel plus iron matrix solution (4.7) to six beakers (150 ml).

7.4.1.2 Add, using a burette (5.2), 0, 1.0, 2.0, 3.0, 5.0 and 10.0 ml respectively of the cobalt standard solution (4.8). Add 20 ml of perchloric acid (4.4) and heat just to the liberation of white fumes. Cool, add 50 ml of water and transfer the solution quantitatively into a 500 ml volumetric flask containing 10 ml of hydrochloric acid (4.1). Add 25 ml of lanthanum solution (4.6), and add water up to the mark and mix.

7.4.2 Set B for calibration solution

7.4.2.1 Transfer six 5 ml volumes of the nickel plus iron matrix solution (4.7) to six beakers (150 ml).

7.4.2.2 Follow 7.4.1.2.

7.5 Preparation of calibration graph and determination

7.5.1 When cobalt content is 0.025 % (*m/m*) or over to and excluding 0.25 % (*m/m*) Carry out the determination on test solution A (7.3.2) and the set of calibration solutions A (7.4.1).

7.5.1.1 Set the required instrument parameters of the atomic absorption spectrometer according to the manufacturer's instructions using a cobalt hollow cathode lamp at a wavelength of 240.7 nm.

7.5.1.2 Light the burner and adjust the air and acetylene flows to obtain a slightly oxidizing clear non-luminescent flame while aspirating water.

7.5.1.3 Aspirate test solution A (7.3.2) into the flame and note the absorbance reading.

7.5.1.4 Aspirate water and check that the reading returns to zero.

7.5.1.5 Aspirate the set of calibration solutions A (7.4.1) in order of increasing instrument response and note the absorbance readings. Flush the system with water between each reading.

7.5.1.6 Aspirate the blank test solution and note the reading.

7.5.1.7 Repeat the measurement of the test solution, blank and calibration solutions to check the repeatability of the readings.

- Remarks 1 Poor repeatability may indicate an instrument malfunction or a variation in the aspiration rate among the solutions.
- 2 Ensure that the measurement corresponding to the test sample falls between two calibration solutions containing cobalt as close as possible to that being determined.

7.5.2 When the expected cobalt content is 0.25 % (m/m) or over up to and including 2.5 % (m/m)

7.5.2.1 Transfer, using a pipette, 25.0 ml of test solution A (7.3.2) into a 250 ml volumetric flask. Add 12 ml of lanthanum solution (4.6), 10 ml of perchloric acid (4.4) and 5 ml of hydrochloric acid (4.1). Make up to the mark with water (test solution B).

7.5.2.2 Dilute the blank test (7.2) as directed in 7.5.2.1.

7.5.2.3 Proceed with the determination as directed in 7.5.1 using test solution B (7.5.2.1), blank test (7.5.2.2) and the set of calibration solution B (7.4.2).

7.6 Preparation of calibration graph Plot the instrument reading for each of the calibration solutions less the reading for the zero member against the concentration of cobalt in the calibration solution.

Remarks : Some instrument may be adjusted to give a read-out directly in concentration of the analyte. A calibration graph of instrument response versus concentration should be plotted to check the linearity and validity of the readings.

8 Expression of results

8.1 Calculation

8.1.1 Determine the concentration of cobalt in the test solution and in the blank from the calibration graph.

8.1.2 The cobalt content, expressed as a percentage by mass, is given by the following formula.

$$C_0 = \frac{V(\rho_1 - \rho_0)}{m} \times 10^{-4} \times f$$

where, C_0 : the content of cobalt [% (m/m)]

ρ_1 : the concentration of cobalt in the test solution (mg/l)