International Standard 7527

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Nickel, ferronickel and nickel alloys — Determination of sulfur content — Iodimetric titration method after induction furnace combustion

Nickel, ferro-nickel et alliages de nickel — Dosage du soufre — Méthode par titrage iodométrique après combustion dans un four à induction

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Foreword

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Nickel, ferronickel and nickel alloys — Determination of sulfur content — Iodimetric titration method after induction furnace combustion

1 Scope and field of application

This International Standard specifies a titrimetric method after combustion for the determination of the sulfur content of nickel and ferronickel in the range 0,001 to 0,3 % (m/m), and of nickel alloys in the range 0,002 to 0,1 % (m/m). Examples of compositions are given in the annex.

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.*

ISO 7525, *Nickel — Determination of sulfur content — Methylene blue molecular absorption spectrometric method after generation of hydrogen sulfide.*

3 Principle

Combustion of a test portion in a flow of oxygen at a high temperature in a high frequency induction furnace in the presence of fluxes and accelerators.

Absorption of the sulfur dioxide formed in an acidified starch-iodide solution and continuous titration with potassium iodate standard volumetric solution.

4 Reagents and materials

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

4.1 Oxygen (O_2), 99,5 % (m/m) minimum.

4.2 Ascarite or **soda lime**, 0,7 to 1,2 mm (14 to 22 mesh).

4.3 Magnesium perchlorate [$Mg(ClO_4)_2$], 0,7 to 1,2 mm (14 to 22 mesh).

4.4 Glass-wool.

4.5 Crucibles and lids.

4.5.1 Ceramic crucibles shall be of precise dimensions so that the sample is positioned correctly in the induction coil of the furnace (see 9.1).

4.5.2 Pre-ignite the crucibles in air or oxygen in a furnace for not less than 1 h at 1 100 °C and store in a desiccator or closed container. A resistance furnace with a combustion tube through which a flow of oxygen passes may be used. Crucible lids, used to help retain the solid oxidation products in the hot zone, are pre-ignited in a similar manner.

4.6 Fluxes: Low sulfur tin, copper plus tin, copper or vanadium pentoxide (see 9.2).

4.7 Accelerators: Low sulfur copper, iron, tungsten or nickel (see 9.2).

4.8 Nickel, low sulfur of known value [$< 0,001$ % (m/m)].

4.9 Standard reference steel, containing 0,1 to 0,2 % (m/m) sulfur.

4.10 Hydrochloric acid, ϱ_{20} = 1,19 g/ml, diluted 1 + 99.

4.11 Starch-iodide, solution.

Transfer 9 g of soluble starch to a 50 ml beaker, add 5 to 10 ml of water and stir until a smooth paste is obtained. Pour the mixture slowly into 500 ml of boiling water. Cool, add 15 g of potassium iodide and stir until it is dissolved. Dilute to 1 litre with water and mix.

4.12 **Potassium iodate,** standard volumetric solution.

Dissolve exactly 0,222 5 g of potassium iodate in 900 ml of water containing 1 g of sodium hydroxide. Transfer to a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

1 ml of this standard volumetric solution is equivalent to 0,1 mg S.

4.13 **Potassium iodate,** standard volumetric solution.

Transfer 200 ml of potassium iodate solution (4.12) to a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

1 ml of this standard volumetric solution is equivalent to 0,02 mg S.

NOTE — The sulfur equivalents of 4.12 and 4.13 are based on the complete conversion and recovery of sulfur as sulfur dioxide. Well-established standards of known sulfur content are used for solution standardization.

5 Apparatus

5.1 The apparatus required for combustion in a high frequency induction furnace and titration of the evolved sulfur dioxide may be obtained commercially from a number of manufacturers. Follow the manufacturer's instructions for the operation of the equipment (see 9.3).

5.2 **Burettes,** of capacity 50 ml, graduated in divisions of 0,1 ml; and of capacity 10 ml, graduated in divisions of 0,02 ml, in accordance with ISO 385/1, class A.

5.3 **Pipettes,** in accordance with ISO 648, class A.

5.4 **Volumetric flasks,** in accordance with ISO 1042, class A.

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 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 portion should be obtained by riffling.

7 Procedure

WARNING — The risks related to combustion analysis are mainly burns in pre-igniting the ceramic crucibles and in the fusions. Use crucible tongs at all times and suitable containers for the used crucibles. Normal precautions for handling oxygen cylinders shall be taken.

7.1 Determination

7.1.1 Weigh, to the nearest 0,001 g, 0,9 to 1,1 g of the test sample, and transfer to a pre-ignited crucible (4.5) containing a suitable amount of the preferred flux (4.6). Add the appropriate quantity of accelerator (4.7), if required. The flux and accelerator used will depend on the individual characteristics of the equipment and the type of material being analysed. Typical additions to a 1,0 g test portion are 2 g of copper, 1 g of copper plus 1 g of iron, 2 to 3 g of tungsten, or 1 g of vanadium pentoxide plus 1 g of iron powder. Place the crucible lid in position.

7.1.2 Place the crucible and contents on the pedestal post of the furnace and, with oxygen flowing, raise to the combustion position.

7.1.3 Add 50 to 70 ml of hydrochloric acid (4.10) and 2 ml of starch-iodide solution (4.11) to the absorption vessel. Add sufficient potassium iodate solution (4.13) from a burette to obtain the intensity of the blue colour which will be taken as the end-point of the final titration. Refill the burette to the zero mark.

NOTE — For sulfur contents higher than 0,02 % (m/m) use the stronger iodate solution (4.12).

7.1.4 Switch on the furnace and combust the sample while passing oxygen through the system. Titrate continuously with the potassium iodate solution (4.13) to maintain the blue starch-iodine colour chosen as the end-point. Do not allow the solution to become colourless at any time during the titration because of possible loss of sulfur dioxide. After the contents of the crucible have combusted completely, as shown by no further decrease of the blue colour, usually after about 5 min, turn off the power supply to the induction coil.

7.1.5 Note the volume of titrant added.

7.1.6 Repeat 7.1.1 to 7.1.5.

7.2 Blank test

7.2.1 Charge a pre-ignited crucible (4.5) with the quantity of flux and accelerator to be used in the determination (7.1) and add 1,00 g of pure nickel of known low sulfur content (4.8).

7.2.2 Proceed as directed in 7.1.2 to 7.1.5.

NOTES

1 The volume of titrant corresponds to the blank due to the crucible, flux, accelerator and sulfur in the pure nickel.

2 The blank should not exceed 0,001 % (m/m) sulfur.

3 If the blank reading is abnormally high, investigate and eliminate the source of contamination.

7.3 Calibration

7.3.1 Select a certified standard reference steel (4.9).

NOTE — For ferronickel, reference materials with a higher sulfur content are used.

7.3.2 Use the certified standard reference steel in conjunction with pure nickel of low sulfur content [< 0,001 % (*m*/*m*)] which is known or has been determined by ISO 7525.

7.3.3 Weigh appropriate proportions of the two materials (7.3.1 and 7.3.2) into a pre-ignited crucible, to cover the high end of the calibration range. Add the preselected amounts of flux and accelerator and combust as directed in 7.1.2 to 7.1.5.

7.3.4 Repeat 7.3.3 to check the repeatability of the reading.

7.3.5 Repeat 7.3.3 with different ratios of the reference sample and pure nickel to provide a calibration check over the required range.

7.3.6 Table 1 illustrates the use of the calibration technique using a certified standard reference steel containing 0,100 % (*m*/*m*) S and a reference nickel sample containing 0,001 % (*m*/*m*) S.

Table 1 — Calibration example

Mass of steel	Mass of nickel	Sulfur content in composite
g	g	% (*m*/*m*)
0,500	0,500	0,050 + 0,000 5
0,300	0,700	0,030 + 0,000 7
0,100	0,900	0,010 + 0,000 9
0	1,000	0,001 0

NOTES

1 It is important that a high temperature be maintained after the sample is fused to ensure complete transfer of the sulfur dioxide from the furnace to the titration vessel.

2 A quiescent combustion is necessary to avoid splashing on to the crucible lid where the fused mass may be removed from the induction heating zone.

7.3.7 Subtract the volume of titrant required for the blank test (7.2) from the volumes of titrant required for each of the calibration standards (7.3.1).

7.3.8 Calculate the mass, in micrograms, of sulfur present in each of the portions of calibration standards combusted and plot against the corresponding volume of titrant corrected for the blank test.

8 Expression of results

8.1 Calculation

8.1.1 Subtract the volume of titrant required for the blank test from the volume required for the test portion.

8.1.2 Read the mass, in micrograms, of sulfur in the test portion from the calibration graph.

8.1.3 The sulfur content, expressed as a percentage by mass, of the test sample is given by the formula

$$\frac{m_1}{m_0} \times 10^4$$

where

m_1 is the mass, in micrograms, of sulfur in the test portion;

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

8.1.4 Report the average of the two results obtained for each test sample.

8.2 Precision

The method specified in this International Standard was subjected to an interlaboratory test programme involving 14 laboratories in six countries. Ten samples were analysed in duplicate, according to the procedure, on two different days.

Repeatability and reproducibility were calculated according to ISO 5725 with the results given in table 2.

9 Notes on procedure and equipment

9.1 Crucibles and lids

Ceramic crucibles are required for containing the sample, any additions which may be necessary and for the subsequent fusion. They shall be of precise dimensions for the system and fit the supporting pedestal post so that the test portion in the crucible is positioned correctly within the induction coil for heating.

Typical dimensions of combustion crucibles are

height	25 mm
external diameter	25 mm
internal diameter	20 mm
wall thickness	2,5 mm
thickness of base	8 mm

Crucibles are pre-ignited at 1 100 °C in oxygen to remove sulfur. Lids, placed on the crucible, help to retain the solid oxidation products in the hot zone of the induction coil. The crucible lids are pre-ignited in a similar manner to the crucibles (see 4.5.2).

Table 2 — Results of statistical analysis

Metal or alloy	Mean sulfur content [% (m/m)]	Within laboratory standard deviation, s_w	Between laboratories standard deviation, s_b	Repeatability, r	Reproducibility, R
Ferronickel					
A22	0,020	0,000 8	0,002 2	0,002 3	0,006 6
A28	0,024	0,000 8	0,001 5	0,002 2	0,004 9
C1	0,024	0,000 6	0,000 7	0,001 7	0,002 6
C2	0,049	0,001 0	0,001 7	0,002 9	0,005 6
C3	0,074	0,000 9	0,004 7	0,002 5	0,014
C4	0,20	0,002 5	0,013	0,007	0,039
Nickel					
YG	0,006 7	0,000 2	0,000 5	0,000 5	0,001 6
YF	0,014	0,000 3	0,001 4	0,000 9	0,004 0
Nickel alloy					
AK (H*)	0,003 2	0,000 5	0,001 4	0,001 3	0,004 1
AO (B*)	0,017 8	0,000 3	0,002 5	0,000 9	0,007 1

* Refers to alloy type in table 5.

9.2 Fluxes and accelerators

9.2.1 A flux addition has the effect of bonding together small particles of sample for more effective furnace coupling and to produce a more fluid melt. Tin, copper plus tin, copper and vanadium pentoxide have been found satisfactory.

9.2.2 Copper, iron, tungsten and nickel are common accelerators. An accelerator addition is made for several reasons:

a) to provide a good coupling medium for induction heating for an otherwise unsatisfactory sample, for example a finely divided sample or material of complex composition;

b) to act as a chemical fuel to increase the combustion temperature;

c) to increase the mass of material in the crucible without increasing the mass of the test portion when it is necessary to use small samples.

Any flux or accelerator shall have a low sulfur content and be used in the calibration procedure. The total blank from all sources (oxygen, refractories, flux and accelerator) shall not exceed 0,001 % (m/m) sulfur.

NOTE — Some materials act as both a flux and an accelerator.

9.3 Features and operation of high frequency induction furnaces

9.3.1 The combustion furnace consists of an induction coil and a high frequency generator. The furnace chamber consists of a silica tube which fits inside the induction coil. A metal plate at the bottom contains the gas inlet and is sealed to the tube by an O-ring. Sulfur dioxide formed during combustion is transferred to the titration vessel through a glass tube.

9.3.2 The titration vessel should be equipped with a photoelectric cell to permit control of the intensity of the blue colour due to starch and iodine through addition of titrant. The intensity of the blue colour may be measured by a galvanometer connected to the photocell. Addition of titrant is then done manually. In some instruments addition of titrant to a predetermined colour intensity is done automatically. It is possible to judge the intensity of the blue colour visually but the precision of the analysis is not as good.

9.3.3 The generator is usually a 1,5 to 2,5 kV·A apparent power unit but the frequency used by various manufacturers may be different. Values of 2 to 6; 15; and 20,0 MHz have been used. The power from the generator is fed to the induction coil which surrounds the silica furnace tube which is usually forced air cooled.

9.3.4 The crucible containing the sample, flux and accelerator is supported on a pedestal post which is precisely positioned so that, when raised, the metal in the crucible is correctly placed within the induction coil for effective coupling when the power is applied.

9.3.5 The induction coil diameter, the number of turns and the furnace chamber geometry and the power of the generator determine the degree of coupling which can occur. These factors are determined by the instrument manufacturer.

9.3.6 The temperature attained during combustion depends on the furnace, and the type and quantity of metal in the crucible. A high temperature (> 1 700 °C) is maintained after the test portion is fused so that the sulfur dioxide may be completely removed from the furnace.

9.3.7 The oxygen supply is purified using tubes packed with ascarite (4.2) and magnesium perchlorate (4.3). The flow rate of oxygen may vary from one instrument to another but is usually about 1,5 l/min.

9.3.8 A glass-wool filter between the furnace chamber and the analyser should be changed as necessary. The furnace chamber, pedestal post and filter trap should be cleaned frequently to remove oxide residues.

10 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

Examples of compositions of nickel, ferronickel and nickel alloys

(This annex does not form part of this International Standard.)

The examples of compositions given in tables 3, 4 and 5 are not to be interpreted as specifications for chemical compositions.

Table 3 — Examples of composition of nickel (%)

Ni + Co	Co (max.)	C (max.)	Cu (max.)	Fe (max.)	S (max.)
99,95	0,1	0,015	0,005	0,02	0,002 5
99,9	0,5	0,03	0,03	0,03	0,03
99,0	1,5	0,15	0,2	0,4	0,01

Table 4 — Examples of composition of ferronickel (%)

Type	Ni	C	Cr (max.)	Cu (max.)	Fe	S (max.)	Si (max.)
LC	15 60	0,005 0,03	0,10	0,20	Rem.	0,03	0,20
MC	15 60	0,03 1,0	0,5	0,20	Rem.	0,10	1,0
HC	15 60	1,0 2,5	2,0	0,20	Rem.	0,40	4,0

NOTE — Co is usually 1/40 to 1/20 of Ni.

Table 5 — Examples of composition of nickel alloys (%) 1)

Alloy 2)	Al	B	C	Co 3)	Cr	Cu	Fe	Mn	Mo	Ni	P	S	Si	Ti	Others
A	—	—	0,30	—	—	28,0 34,0	2,5	2,0	—	63,0 4)	—	0,025	0,5	—	—
B	—	—	0,15	—	14,0 17,0	0,5	6,0 10,0	1,0	—	72,0 4)	—	0,015	0,5	—	—
C	0,4 1,0	—	0,08	—	14,0 17,0	0,5	5,0 9,0	1,0	—	70,0 4)	—	0,015	0,5	2,2 2,8	Nb plus Ta 0,7 to 1,2
D	0,2 0,8	0,006	0,08	—	17,0 21,0	0,3	Rem.	0,4	2,8 3,3	50,0 55,0	0,015	0,015	0,4	0,6 1,2	Nb plus Ta 4,7 to 5,5
E	0,15 0,60	—	0,10	—	19,0 23,0	0,7	Rem.	1,5	—	30,0 35,0	—	0,015	1,0	0,15 0,60	—
F	—	—	0,08 0,15	5,0	18,0 21,0	0,5	5,0	1,0	—	Rem. 4)	—	0,020	1,0	0,2 0,6	Pb 0,005
G	1,0 2,0	0,020	0,13	15,0 21,0	18,0 21,0	0,2	1,5	1,0	—	Rem.	—	0,015	1,0	2,0 3,0	Zr 0,15
H	4,5 4,9	0,003 0,010	0,12 0,17	18,0 22,0	14,0 15,7	0,2	1,0	1,0	4,5 5,5	Rem.	—	0,015	1,0	0,9 1,5	Zr 0,15
I	0,3 0,6	0,005	0,04 0,08	19,0 21,0	19,0 21,0	0,2	0,7	0,6	5,6 6,1	Rem.	—	0,007	0,4	1,9 2,4	Ti plus Al 2,4 to 2,8
J	—	—	0,02	1,0	1,0	—	2,0	1,0	26,0 30,0	Rem. 4)	0,040	0,035	0,1	—	—
K	1,2 1,6	0,003 0,010	0,02 0,10	12,0 15,0	18,0 21,0	0,1	2,0	1,0	3,5 5,0	Rem.	0,015	0,015	0,1	2,8 3,3	Zr 0,02 to 0,08
L	—	—	0,02	2,5	14,5 16,5	—	4,0 7,0	1,0	15,0 17,0	Rem.	0,040	0,035	0,08	—	V 0,35 W 3,0 to 4,5

1) Single values are maximum limits, except for nickel, where single values are minimum.

2) Alloy letters are used instead of commercial names until a neutral ISO designation is developed.

3) Where no limits are given, cobalt is up to a maximum of 1,5 % (*m*/*m*).

4) Cobalt counts as nickel in some alloys.