International Standard 7526

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Nickel, ferronickel and nickel alloys — Determination of sulfur content — Infra-red absorption method after induction furnace combustion

Nickel, ferro-nickel et alliages de nickel — Dosage du soufre — Méthode par absorption dans l'infrarouge 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 — Infra-red absorption method after induction furnace combustion

1 Scope and field of application

This International Standard specifies an infra-red absorption 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 0,001 to 0,1 % (m/m). Examples of compositions are given in annex A.

NOTE — It may be possible to apply this method in the range 0,000 2 to 0,001 % (m/m). However, there were insufficient laboratory test data to support the inclusion of this lower level in the scope.

2 References

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.

Measurement of the sulfur dioxide formed using an infra-red analyser and an integration procedure.

4 Reagents and materials

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 steels, containing 0,1 to 0,2 % (m/m) sulfur.

5 Apparatus

The apparatus required for combustion in a high frequency induction furnace and the subsequent infra-red absorption measurement 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. A pressure regulator is required to control the oxygen pressure to the furnace according to the manufacturer's specification (usually 28 kN/m^2). Features of commercial equipment are given in annex B.

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. Oxygen from the combustion process shall be removed effectively from the apparatus since a high concentration of oxygen in a confined space can present a fire hazard.

7.1 Stabilizing the equipment

7.1.1 Condition and stabilize the equipment by combusting several samples, similar to those to be analysed (7.4), using appropriate fluxes and accelerators.

NOTE — It is not necessary to use pre-ignited crucibles.

7.1.2 Allow the instrument to cycle several times with oxygen flowing and adjust the instrument zero.

7.2 Blank test and zero adjustment

7.2.1 Charge a pre-ignited crucible (4.5) with the quantity of flux and accelerator to be used in the determination (7.4) and add 1,00 g of pure nickel of known low sulfur content (4.8).

7.2.2 Place the crucible and contents on the pedestal post of the furnace, raise to the combustion position and lock the system. Operate the furnace in accordance with the manufacturer's instructions. See 9.3 and annex B.

NOTES

1 The reading obtained 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.

7.2.3 Adjust the instrument reading using the zero adjust or, on some instruments, the blank offset control, to read the sulfur value of the nickel (4.8).

7.2.4 Repeat 7.2.1 to 7.2.3 to obtain a reproducible reading within the precision limits of the instrument.

NOTE — An alternative procedure is to record the reading of the blank test and make the correction using a calibration graph.

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 in 7.2.2. Note the instrument reading.

7.3.4 Adjust the instrument reading to correspond to the correct level of sulfur in the mixture (7.3.3) according to the manufacturer's operating instructions.

7.3.5 Repeat 7.3.3 to check the repeatability of the reading.

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

7.3.7 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

7.4 Determination

7.4.1 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.

7.4.2 Place the crucible and contents on the pedestal post of the furnace, raise to the combustion position and lock the system. Operate the furnace in accordance with the manufacturer's instructions. See 9.3 and annex B.

7.4.3 Record the analyser reading and repeat the determination.

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 infra-red analyser.

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.

8 Expression of results

8.1 Calculation

8.1.1 If the instrument has been calibrated to give a read-out directly as a percentage by mass of sulfur with automatic compensation for the mass of the test portion, take the average of the two determinations and report the result.

8.1.2 If the instrument has been calibrated based on a 1,00 g test portion and does not have automatic mass compensation, divide each reading by the respective mass, in grams, of the test portion. Average the two determinations and report the result.

8.1.3 With some instruments it will be necessary to prepare a calibration graph of instrument reading versus the mass, in micrograms, of sulfur. Read off the graph the mass, in micrograms, of sulfur in the test portion, correct for the blank and mass of the test portion. Average the two determinations and report the result.

8.2 Precision

The method specified in this International Standard was subjected to an interlaboratory test programme involving 14 laboratories in six countries. Eleven 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.

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.

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 6	0,001 3	0,001 8	0,004 0
A28	0,023	0,000 3	0,001 7	0,000 9	0,005 0
C1	0,024	0,000 5	0,001 0	0,001 4	0,003 2
C2	0,048	0,000 7	0,003 0	0,002 1	0,008 9
C3	0,074	0,000 9	0,003 1	0,002 5	0,009 1
C4	0,20	0,003 3	0,013	0,009	0,038
Nickel					
HN *	0,000 4	0,000 14	0,000 15	0,000 4	0,000 5
YG	0,006 3	0,000 2	0,000 5	0,000 5	0,001 6
YF	0,013	0,000 3	0,001 3	0,000 7	0,003 8
Nickel alloy					
AK (H**)	0,002 5	0,000 2	0,000 6	0,000 6	0,001 9
AO (B**)	0,016	0,000 6	0,001 0	0,001 8	0,003 3

* Below scope, included for information.

** Refers to alloy type in table 5.

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 Features of commercial equipment are given in annex B.

9.3.2 Purify the oxygen supply using tubes packed with ascarite (4.2) and magnesium perchlorate (4.3) and maintain a flow rate of about 0,5 l/min while on stand-by.

9.3.3 Maintain a glass-wool filter between the furnace chamber and the analyser and change as necessary. The furnace chamber, pedestal post and filter trap should be cleaned frequently to remove oxide residues.

9.3.4 The manufacturer may recommend setting the programming unit to give a pre-burn period before oxygen enters the furnace chamber. The test portion should be at a red heat during the pre-burn period. When oxygen is introduced for the combustion stage the temperature increases substantially.

9.3.5 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 to the infra-red analyser.

9.3.6 The flow rate of oxygen may vary from one instrument to another but is usually about 2,0 l/min during the combustion period.

9.3.7 After the equipment has been idle for a few hours or after cleaning the furnace chamber or filters, the instrument should be stabilized as directed in 7.1.

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 A

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.

Annex B

Features of commercial high frequency induction furnaces and infra-red sulfur analysers

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

B.1 Combustion furnace

B.1.1 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. This tube has metal plates at the top and bottom which are sealed to the tube by O-rings. Gas inlet and outlet points are made through the metal plates.

B.1.2 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 and is usually air cooled.

B.1.3 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.

B.1.4 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.

B.1.5 The temperature attained during combustion depends in part on the factors in B.1.4 but also on the characteristics of the metal in the crucible, the form of the test portion and the mass of material. Some of these factors may be varied to some extent by the operator.

B.2 Infra-red gas analyser

B.2.1 In most instruments the gaseous products of combustion are transferred in a continuous flow of oxygen to the analyser system. The gases flow through an infra-red cell, for example of the Luft type, where the absorbance of the infra-red radiation due to sulfur dioxide is measured and integrated over a pre-programmed time period. The signal is amplified and converted to a digital display of the percentage concentration of sulfur.

B.2.2 In some analysers the products of combustion may be collected in oxygen in a fixed volume at controlled pressure and the mixture analysed for sulfur dioxide.

B.2.3 Electronic controls are usually provided for adjusting the instrument zero, compensating for the blank, adjusting the slope of the calibration line and correction for non-linear response. The analyser generally has means of entering the mass of the standard or test portion for automatic correction of the read-out. Instruments may also be equipped with an integrated automatic balance for weighing the crucible, weighing the test portion and transferring the mass to the analyser.