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Ferronickels — Determination of sulfur content — Infrared absorption method after induction furnace combustion

Ferronickels — Détermination de la teneur en soufre — Méthode par absorption dans l'infrarouge après combustion dans un four à induction

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/SS M14, *Nickel*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 7526:1985), which has been technically revised. The main changes compared with the previous edition are as follows:

- the scope has been limited to ferronickels only;
- the former Clauses 5 and 7 have been technically revised;
- the former Annexes A and C have been deleted;
- the precision data have been updated.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Ferronickels — Determination of sulfur content — Infrared absorption method after induction furnace combustion

1 Scope

This document specifies an infrared absorption method after combustion in an induction furnace for the determination of the sulfur content in ferronickels in the range of 0,002 % to 0,12 %.

The method is applicable to normal production operations. It uses commercially available equipment, which is calibrated using steel and/or ferronickel certified reference materials (CRMs).

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

Combustion of a test portion in a high-frequency induction furnace at high temperature in a current of pure oxygen, and in the presence of accelerators and fluxes.

Transformation of sulfur into sulfur dioxide.

Measurement by infrared absorption of the sulfur dioxide carried by the current of oxygen.

5 Reagents

During the analysis, use only reagents of recognized analytical grade.

5.1 Oxygen, high purity (mass fraction minimum 99,5 %).

An oxidation catalyst [copper(II) oxide or platinum] tube heated at 600 °C, followed by appropriate carbon dioxide and water absorbents, shall be used when the presence of organic contaminants is suspected in the oxygen.

5.2 Inert ceramic (attapulgus clay), impregnated with sodium hydroxide and having particle sizes from 0,7 mm to 1,2 mm for the absorption of carbon dioxide.

5.3 Magnesium perchlorate [$Mg(ClO_4)_2$], having particle size from 0,7 mm to 1,2 mm for the absorption of moisture.

5.4 Glass-wool.

5.5 Fluxes and accelerators.

5.5.1 General

A flux addition has the effect of bonding together small particles for more effective furnace coupling and it helps to produce a more fluid melt.

An accelerator addition allows:

a) a good coupling medium for the induction heating of otherwise unsatisfactory samples (finely divided samples, materials of complex composition);

b) a higher combustion temperature;

c) an increase of the mass of material in the crucible when the test portions are small.

Any flux or accelerator shall have low sulfur content and shall be used in the calibration procedure. The total blank from all sources (oxygen, refractories, flux and accelerator) shall not exceed 0,000 5 % (mass fraction) sulfur.

Some materials act as both a flux and an accelerator.

5.5.2 Fluxes

Common fluxes are tin, copper plus tin, copper or vanadium pentoxide.

5.5.3 Accelerators

Common accelerators are copper, iron, tungsten or nickel.

5.6 Steel and/or ferronickel certified reference materials (CRMs), containing from 0,001 % to 0,15 % (mass fraction) sulfur.

All reference materials used for calibration shall be certified by internationally recognized bodies. Preference shall be given to materials that are certified using referee methods, e.g. ISO 4934, ISO 4935, ISO 10701 and ISO 13902, traceable to SI units as opposed to those based on other certified reference materials.

6 Apparatus

Usual laboratory apparatus and, in particular, the following.

6.1 Sulfur analyser.

6.1.1 The apparatus required for combustion in a high frequency induction furnace and the subsequent infrared 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.

6.1.2 Purify the oxygen supply using tubes packed with inert ceramic (5.2) and magnesium perchlorate (5.3) and maintain a flow rate of about 0,5 l/min while on stand-by.

6.1.3 Maintain a glass-wool filter (5.4) 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.

6.1.4 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.

6.1.5 The temperature reached 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 can be completely removed from the furnace to the infrared analyser.

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

6.1.7 After the equipment has been idle for a few hours or after cleaning the furnace chamber or filters, the instrument should be stabilized as described in 8.1.

NOTE Features of commercial equipment are given in Annex A.

6.2 Ceramic crucibles and lids.

Ceramic crucibles, containing the sample and any additions that can be necessary, are required for the combustion. 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: a height of 25 mm, an external diameter of 25 mm, an internal diameter of 20 mm, a wall thickness of 2,5 mm, and a thickness of base of 8 mm. The dimension of the hole of the lid should be larger than 10 mm.

Crucibles and lids shall be as specified by the manufacturer of the instrumentation used and shall be capable of withstanding combustion in an induction furnace without evolving sulfur-containing chemicals so that achieving and maintaining blank values within specification is possible.

In order to remove any sulfur contamination, 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 a closed container. A resistance furnace with a combustion tube through which a flow of oxygen passes may also be used.

Crucible lids, used to help retain the solid oxidation products in the hot zone of the induction coil, shall be pre-ignited in a similar manner.

6.3 **Crucible tongs,** capable of handling recommended crucibles (6.2).

7 Sampling and sample preparation

7.1 Sampling and sample preparation shall be carried out by normal agreed procedures or, in cases of dispute, by appropriate national standards.

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

7.3 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.

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

8 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 appropriate 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.

8.1 Preparing and stabilizing the instrument

8.1.1 Assemble the apparatus and prepare it for operation according to the manufacturer's instructions. Test the furnace and analyser to ensure the absence of leaks.

8.1.2 Condition and stabilize the equipment by combusting several samples, similar to those to be analysed, using appropriate fluxes and accelerators, before attempting to calibrate the system or determine the blank.

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

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

8.2 Blank test and zero adjustment

8.2.1 Sulfur contents ≤ 0,05 %

For each instrument range, transfer the selected mass of flux (5.5.2), to the nearest 0,005 g, into a pre-ignited crucible (6.2), add the selected mass of a CRM (5.6) having a very low sulfur content, and then cover it with the selected mass of accelerator (5.5.3).

The type and mass of the flux and accelerator used in the blank test should accord with those used for the determinations (details as in 8.4.1). Record the mass of the CRM. Place the crucible and contents on the furnace pedestal and operate the furnace in accordance with the manufacturer's instructions. Repeat the determination three more times. Average the results.

Subtract the sulfur content of the CRM from the average to determine the blank value. If the blank is greater than 0,001 % (mass fraction) and the related standard deviation is greater than 0,000 2 % (mass fraction), find the cause of the problem, fix it and repeat the experiment.

Record the average blank value into the analyser in accordance with the manufacturer's instructions.

NOTE 1 The reading obtained corresponds to the blank due to the crucible, flux and accelerator.

If the analyser does not have automatic blank correction, the blank value should be subtracted from the total result prior to any calculation.

NOTE 2 An alternative procedure is to record the reading of the blank test and make the correction using a calibration graph.

8.2.2 Sulfur contents > 0,05 %

It is preferable not to carry out a blank correction. However, a check of the blank level shall be done. The value shall remain below 0,000 5 % (mass fraction).

8.3 Calibration

8.3.1 Select a set of steel and/or ferronickel CRMs (5.6) for calibration and verification which, at a minimum, fall at the bottom, top, and quartile points of each operational operating range.

8.3.2 If the instrument has more than one sulfur detector (measurement system), carry out the adjustment described in this section on each one.

Establish all experimental parameters for each range of sulfur. Parameters to be specified include:

- crucible: to be pre-burned or not;
- flux and accelerator: type and mass;
- test portion: mass.

8.3.3 For each detector (see 8.3.2) weigh an appropriate amount (usually 0,50 g) of a CRM having a sulfur content corresponding to the top of each operating range into a pre-ignited crucible (6.2). Add the pre-selected amounts of flux (5.5.2) and accelerator (5.5.3) and combust as described in 8.4.1. Repeat this process twice.

If the results are situated in the interval “Certified Value ± 2σ”, adjust the net instrument reading to correspond to the certified content of sulfur in the reference material, according to the manufacturer’s instructions.

8.3.4 Check the linearity of the calibration by analysing at least three times a CRM having a sulfur content in the middle of the range of the detector. The result shall be situated in the interval “Certified Value ± 2σ”.

Correct any non-compliant conditions before continuing to the next step.

8.4 Determination

8.4.1 Weigh, to the nearest 0,001 g, 0,5 g to 0,6 g of the test sample, and transfer into a pre-ignited crucible (6.2) containing an appropriate amount of the selected flux (5.5.2), if required. Then cover the test sample with the appropriate quantity of accelerator (5.5.3) and, if necessary, place the lid on the crucible.

NOTE The flux and accelerator used will depend on the individual characteristics of the equipment and the type of material being analysed. For ferronickels, 1,0 g to 1,5 g of tungsten plus tin (7 to 9 parts of tungsten + 1 part of tin) can be used.

8.4.2 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.

8.4.3 Record the analyser reading and repeat the determination at least once.

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

NOTE 2 Quiescent combustion is necessary to avoid splashing on to the crucible lid.

8.4.4 Analyse, at least twice, CRMs having sulfur contents slightly above and slightly below the content found for each unknown sample. The corresponding result shall be situated in the interval “Certified Value ± 2σ”. The CRMs used for checking the accuracy of the determination shall be different from those used for the calibration (see 8.3).

8.4.5 If abnormal deviations appear, reject the results and restart the procedures described in 8.3 and 8.4.

9 Expression of results

9.1 Calculation

9.1.1 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 set of determinations carried out and report the result.

9.1.2 If the instrument has been calibrated based on a 0,50 g test portion and does not have automatic mass compensation, divide each reading by the respective mass, expressed in grams, of the test portion. Average the determinations carried out and report the mean result.

9.1.3 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, expressed in micrograms, of sulfur in the test portion, correct for the blank and mass of the test portion. Average the determinations carried out and report the result.

9.2 Precision

Fourteen laboratories in four countries participated in an inter-laboratory validation test programme under the auspices of ISO/TC 155 involving three determinations of sulfur at seven content levels (samples).

Each laboratory carried out two determinations under repeatability conditions as defined in ISO 5725-1, i.e. one operator, same apparatus, identical operating conditions, same calibration and a minimum period of time. The third determination was carried out at a different time using the same apparatus with a different calibration.

The compositions of the samples used are given in Annex B.

The results obtained were statistically evaluated in accordance with ISO 5725-2 and ISO 5725-3. They are reported in Table 1, which shows that the reproducibility (R) corresponding to a sulfur content of 0,276 % is higher than the acceptable level (compare CV (R) % to Max CV (R) %). Therefore, the scope of the method was reduced to sulfur contents ≤ 0,12 %.

For the range 0,002 % to 0,12 %, the logarithmic relationships between the sulfur content (m) and the precision parameters (r, R_w and R), together with the corresponding correlation coefficients are:

$\lg r = 0{,}779 \lg m - 1{,}542$ [correlation coefficient = 0,924]

$\lg R_w = 0{,}709 \lg m - 1{,}365$ [correlation coefficient = 0,970]

$\lg R = 0{,}755 \lg m - 1{,}110$ [correlation coefficient = 0,954]

The corresponding graphical representation is shown in Annex C.

The smoothed values of the repeatability limit (r) and reproducibility limits (R_w and R) of the test results are summarized in Table 2.

Table 1 — Results obtained from the precision test

Sample (%)	**Ferronickel 1**	**Ferronickel 2**	**Ferronickel 3**	**Ferronickel 4**	**Ferronickel 5**	**Ferronickel 6**	**Ferronickel 7**
Mean	0,272 9	0,111 0	0,048 5	0,012 6	0,009 36	0,001 99	0,039 6
σ (r)	0,003 9	0,001 2	0,001 9	0,000 5	0,000 32	0,000 05	0,000 6
σ (R_w)	0,005 1	0,003 5	0,001 7	0,000 6	0,000 38	0,000 24	0,002 1
σ (R)	0,021 8	0,006 7	0,002 5	0,000 8	0,000 49	0,000 38	0,002 9
r	0,010 8	0,003 2	0,005 3	0,001 3	0,000 90	0,000 16	0,001 6
$\mathrm{R_w}$	0,014 2	0,009 7	0,004 7	0,001 7	0,001 07	0,000 68	0,005 8
R	0,061 0	0,018 9	0,007 1	0,002 3	0,001 37	0,001 06	0,008 1
CV (R)	7,98	6,08	5,22	6,54	5,23	19,1	7,34
Aim CV (R)	2,32	3,17	4,22	6,73	7,46	12,8	4,52
Max CV (R)	5,09	6,97	9,27	14,9	16,4	28,0	9,94
Assigned value	0,276	0,113	0,049	0,013	0,009 5	0,002 0	0,04

Values in per cent

Table 2 — Smoothed values of the repeatability and reproducibility limits

Sulfur content	r	R_w	R
0,002	0,000 2_3	0,000 5_3	0,000 7_1
0,005	0,000 4_6	0,001 0_1	0,001 4_2
0,01	0,000 8	0,001 7	0,002 4
0,02	0,001 4	0,002 7	0,004 1
0,05	0,002 8	0,005 2	0,008 1
0,10	0,004 8	0,008 4	0,013 7
0,12	0,005 5	0,009 6	0,015 7

10 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample and the laboratory;

b) the method used by reference to this document, i.e. ISO 7526;

c) the results and the unit in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this document, or any optional operation which may have influenced the results;

f) signature of the responsible person;

g) the date of the test and/or date of preparation or signature of the test report.

Annex A
(informative)

Features of commercial high frequency induction furnaces and infrared sulfur analysers

A.1 Combustion furnace

A.1.1 The combustion furnace consists of an induction coil and a high frequency generator. The furnace chamber consists of a silica tube that 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.

A.1.2 The generator is usually a 1,5 kV.A to 2,5 kV.A apparent power unit but the frequency used by various manufacturers may be different. Values of 2 MHz to 6 MHz, 15 MHz 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 forced air cooled.

A.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.

A.1.4 The induction coil diameter, the number of turns and the furnace chamber geometry, and the power of the generator define the degree of coupling that can occur. These factors are defined by the instrument manufacturer.

A.1.5 The temperature attained during combustion depends in part on the factors given in A.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.

A.2 Infrared gas analyser

A.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 infrared cell, for example of the Luft type, where the absorbance of the infrared 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.

A.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.

A.2.3 Electronic controls are usually provided for adjusting the zero of the instrument, compensating for the blank, adjusting the slope of the calibration line and correcting for the nonlinear response. The analyser generally has means of entering the mass of the samples for an automatic correction of the read-out. Instruments may also be equipped with an integrated automatic balance for weighing the crucibles, weighing the samples and transferring the mass to the analyser.

Annex B
(informative)

Composition of the samples used for the validation precision test

The compositions of the samples used for the validation precision test are listed in Table B.1.

Table B.1 — Compositions of the samples used for the validation precision test

Sample no.	S	C	Si	P	Cr	Ni	Co	Cu	Fe
Ferronickel 1	0,276	2,50	1,04	0,020	1,94	14,96	0,98	0,117	77,85
Ferronickel 2	0,113	1,02	0,39	0,032 5	1,49	18,63	0,60	0,049	77,66
Ferronickel 3	0,049	1,45	0,22	0,011	1,08	25,95	0,46	0,015	70,74
Ferronickel 4	0,013	0,474	1,64	0,006 0	0,72	30,77	1,27	0,140	64,66
Ferronickel 5	0,009 5	0,096	3,33	0,009 2	0,36	40,54	1,87	0,191	52,77
Ferronickel 6	0,002 0	0,036	4,49	0,004 2	0,133	49,07	2,01	0,250	42,74
Ferronickel 7	0,04	0,0044	0,25	0,021	0,46	33,26	0,45	0,072	