INTERNATIONAL STANDARD

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Nickel and nickel alloys — Determination of total boron content — Curcumin molecular absorption spectrometric method

Nickel et alliages de nickel — Dosage du bore total — Méthode par spectrométrie d'absorption moléculaire à la curcumine

Reference number
ISO 11436:1993(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11436 was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*, Sub-Committee SC 4, *Analysis of nickel alloys*.

Annex A of this International Standard is for information only.

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Nickel and nickel alloys — Determination of total boron content — Curcumin molecular absorption spectrometric method

1 Scope

This International Standard specifies a molecular absorption spectrometric method for the determination of the total boron content in the range of 4 g/t to 240 g/t in nickel and nickel alloys.

NOTE 1 A possible chemical interference from rhenium has been identified.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

3 Principle

Dissolution of a test portion in hydrochloric and nitric acids. Decomposition of resistant boron compounds (e.g. boron nitrides) by fuming the sample solution with phosphoric and sulfuric acids at not less than 290 °C for 30 min.

Formation of the boron curcumin complex in a buffered acetic acid and sulfuric acid medium, and measurement of the absorbance of the test solution at a wavelength of 543 nm.

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 Hydrochloric acid, ρ_{20} = 1,18 g/ml.

4.2 Sulfuric acid, ρ_{20} = 1,84 g/ml.

4.3 Nitric acid, ρ_{20} = 1,41 g/ml.

4.4 Phosphoric acid, ρ_{20} = 1,71 g/ml.

4.5 Sodium hypophosphite, monohydrate ($NaH_2PO_2.H_2O$).

4.6 Acetic acid, glacial, ρ_{20} = 1,05 g/ml.

The reagent must be free from aldehydes.

Aldehyde test procedure: Transfer 20 ml of the acetic acid to a 50 ml beaker and add 1 ml of 1 g/l potassium permanganate solution. The colour should not disappear within 10 min. If aldehydes are present, an easily visible brown colour will develop in 15 min.

4.7 Acetic acid-sulfuric acid mixture, 1 + 1.

Add in small portions, while stirring and cooling under running water, one volume of the sulfuric acid (4.2) to one volume of the acetic acid (4.6).

4.8 Acetate buffer, solution.

Dissolve 225 g of ammonium acetate (CH_3COONH_4) in 400 ml of water. Add 300 ml of the acetic acid (4.6). Filter the solution through a medium filter paper and dilute to 1 000 ml. Store in a polyethylene bottle.

4.9 Sodium fluoride, solution.

Dissolve 4 g of sodium fluoride (NaF) in 100 ml of water and mix.

4.10 Boron, standard reference solution (100 mg/l).

Weigh, to the nearest 0,000 1 g, 0,285 8 g of boric acid (H_3BO_3) and transfer it to a 500 ml one-mark volumetric flask. Dissolve the acid in water, make up to the mark and mix. Store the solution in a polyethylene flask.

4.11 Boron, standard solution (2 mg/l).

Transfer 20,0 ml of the boron stock solution (4.10) to a 1 000 ml one-mark volumetric flask. Dilute to volume with water and mix. Store the solution in a polyethylene flask. Prepare freshly before use.

4.12 Curcumin, solution.

Dissolve 0,125 g of curcumin ($C_{26}H_{20}O_6$) in 60 ml of the acetic acid (4.6) in a polyethylene or quartz vessel, by heating in a water bath and using a magnetic stirrer. Cool and transfer to a 100 ml plastics volumetric flask (5.3). Dilute to volume with the acetic acid (4.6) and mix.

This solution must be prepared freshly before use.

5 Apparatus

All glassware and plastics flasks used in this method must be rinsed first with the acetic acid (4.6), then with water and finally dried.

5.1 Quartz conical flasks, of capacity 100 ml, with quartz or polypropylene covers.

5.2 Aluminium alloy block, recommended but not essential, which allows a temperature of 290 °C to be achieved and sustained throughout the fuming period. The block (see figures A.1, A.2 and A.3) has holes designed to fit the 100 ml quartz flasks exactly and is heated by surface contact with a hotplate which enables the temperature of the aluminium block to be controlled up to about 320 °C.

5.3 Plastics volumetric flasks, of capacity 50 ml and 100 ml.

5.4 Plastics flasks, of capacity 100 ml, 500 ml and 1 000 ml.

5.5 Molecular absorption spectrometer, capable of measuring absorbance at a wavelength of 543 nm using a spectral bandwidth of 10 nm or less. The wavelength setting shall be accurate to ± 2 nm, as measured by the absorption maximum of a holmium oxide filter at 536 nm or by another suitable calibration method. The precision of the absoprtion measurement for the solution of highest absorbance shall have a repeatability, expressed as relative deviation, of ± 0,3 % or better.

6 Sampling and sample preparation

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

6.2 The laboratory sample is normally in the form of 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 dried in air.

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

7 Procedure

7.1 Preparation of the aluminium block

Place the aluminium block on a heat source. Adjust the surface temperature of the source, until a constant temperature is reached in the range of 280 °C to 320 °C, in a test flask containing 10 ml of sulfuric acid (4.2). (The temperature can be measured with a thermometer graduated from 0 °C to 350 °C.)

NOTE 2 Equivalent results can be obtained without an aluminium block, provided that the temperature of each vessel is measured with a thermometer in a sleeve and is maintained at a minimum of 290 °C.

7.2 Test portion and preparation of test solution

7.2.1 Weigh to the nearest 0,001 g approximately

— 0,5 g of the test sample, for contents less than 120 g/t;

— 0,25 g of the test sample, for contents between 120 g/t and 240 g/t.

7.2.2 Place the test portion in the 100 ml quartz conical flask (5.1). Add 10 ml of the hydrochloric acid (4.1) and 5 ml of the nitric acid (4.3). Place the quartz or polypropylene cover on the flask and leave it at ambient temperature in order to avoid possible loss of boron at higher temperatures. Wait until dissolution is complete or until effervescence ceases. Swirl occasionally when samples are difficult to dissolve.

7.2.3 Carefully add 10 ml of the phosphoric acid (4.4) and 5 ml of the sulfuric acid (4.2). Place the quartz flask without its cover in a hole in the hot aluminium alloy block. Heat until the sulfuric acid starts to fume, replace the cover and continue heating for 30 min. Remove the flask from the block and allow to cool. Dilute the syrupy solution with 30 ml of water. Warm and stir.

7.2.4 Add 5 ml of the hydrochloric acid (4.1) and bring to boiling. Add 3 g of sodium hypophosphite (4.5) and allow to boil gently for 15 min. Remove from the heat source and allow to cool. Transfer the solution quantitatively to a 50 ml plastics volumetric flask (5.3). Dilute to volume with water and mix.

NOTE 3 In test solutions made from samples containing copper, a precipitate will appear. This precipitate will not interfere if it is allowed to settle before an aliquot is taken.

7.3 Sample compensating solution

Transfer 1,0 ml of the test solution (7.2.4) to a 100 ml plastics flask (5.4). Add 0,2 ml of the sodium fluoride solution (4.9), avoiding contact with the flask wall. Carefully swirl the small volume of solution and allow to stand for 1 h. Continue with the colour development as directed in 7.4.2.

NOTE 4 This solution should be ready before the colour development step is started, since the curcumin complex solution and the compensation solution should be ready for measurement at the same time.

7.4 Colour development

7.4.1 Transfer 1,0 ml of the test solution (7.2.4) to a 100 ml plastics volumetric flask (5.3).

7.4.2 Add the following quantities of reagents to the two flasks (7.3 and 7.4.1) and mix after each addition by swirling to avoid contact with the stoppers.

— 6,0 ml of the acetic acid-sulfuric acid mixture (4.7). Avoid contact of the pipette with the neck and sides of the flask.

— 6,0 ml of the curcumin solution (4.12). Stopper the flask and **allow to stand for 2 h 30 min** for complete development of the colour.

— 1,0 ml of the phosphoric acid (4.4) to stabilize the colour. Shake and **allow to stand for 30 min.**

— 30,0 ml of the acetate buffer solution (4.8). The solution becomes orange. Stopper and shake. **Allow to stand for exactly 15 min.**

NOTE 5 In order to carry out the spectrometric measurements on all the solutions, whilst keeping exactly to the final waiting time of 15 min after the addition of the acetate buffer solution, it is advisable to group the solutions into series of six measurements. If the waiting time is not strictly adhered to, formation of a cloudiness in the solutions may be observed and, consequently, erroneous results obtained.

7.5 Spectrometric measurement

7.5.1 Using 2 cm cells, measure the absorbance of the boron curcumin complex test solution (from 7.4.1) and the corresponding compensating solution (from 7.3) against water as the reference, at a wavelength of 543 nm with the molecular absorption spectrometer (5.5).

7.5.2 Subtract the absorbance of the compensating solution from the absorbance of the test solution containing the boron curcumin complex.

7.6 Blank test

Carry out a reagent blank test in parallel with the determination, following the same procedure and using the same quantities of all the reagents. Subtract the measured absorbance of the blank compensating solution from the absorbance of the blank solution.

7.7 Calibration

7.7.1 Using a burette, transfer the boron standard solution (4.11) as indicated in the table 1, to a series of six 100 ml quartz conical flasks (5.1).

Continue as directed for the test sample in 7.2.2 through 7.5, omitting 7.3.

7.7.2 Subtract the absorbance of the first "zero" member from each solution containing boron, and plot the net absorbance against the mass, in micrograms, of boron in the measured solution.

NOTE 6 The compensation solutions (7.3) do not have to be prepared, since all solutions have the same matrix.

7.8 Number of determinations

Carry out the determination at least in duplicate.

8 Expression of results

8.1 Calculation

8.1.1 Convert the net absorbances of the test solution (7.5.2) and of the blank test (7.6) into micrograms of boron using the calibration graph (see 7.7.2).

8.1.2 Calculate the boron content w_B, expressed in grams per tonne, of the test portion using the formula

$$w_B = \frac{m_1 - m_2}{m_0}$$

where

m_0 is the mass, in grams, of the test portion (see 7.2.1);

m_1 is the mass, in micrograms, of boron found in the test portion;

m_2 is the mass, in micrograms, of boron in the blank test.

8.2 Precision

8.2.1 Laboratory tests

Nine laboratories in four countries participated in the testing of this procedure using four samples of nickel alloys and two certified reference materials. The samples were analysed in duplicate on two different days. The nominal composition of the samples is given in table 2.

Table 1 — Boron calibration solutions

Boron standard solution (4.11) ml	**Corresponding mass of boron** µg	**Boron range covered in the sample** (g/t)	
		Test portion = 0,5 g	**Test portion** = 0,25 g
0	0	4 to 120	10 to 240
1,0	2		
5,0	10		
10,0	20		
20,0	40		
30,0	60		

Table 2 — Composition of test samples [% (*m/m*)]

Sample	B	Co	Cr	Fe	Mo	Nb	Ta	Ti	V	W	Ni
Nominal composition											
1	0,000 5	—	20	48	—	—	—	—	—	—	Remainder
2	0,002	—	19	20	3	5	—	1	—	—	Remainder
3	0,003	—	16	8	—	—	—	—	—	—	Remainder
4	0,008	8	16	—	2	1	2	4	—	2	Remainder
Certified reference materials											
BAM 285-1	0,000 6	9,22	0,034	—	5,07	—	—	0,74	—	—	18,46
BCS 345	0,019	14,70	9,93	—	3,01	—	—	4,74	1,00	—	Remainder

8.2.2 Statistical analysis

8.2.2.1 Results from the interlaboratory test programme were evaluated according to ISO 5725, using the means of the duplicate results. The data were tested for statistical outliers by the Cochran and Dixon tests given in ISO 5725.

8.2.2.2 The principle of the Cochran test is that a set of results is an outlier if the within-laboratory variance is too large in relation to others. Dixon's test is to determine if the mean from a laboratory is too far from the other laboratory means. Both tests were applied at the 95 % confidence level.

8.2.2.3 Repeatability and reproducibility were calculated according to ISO 5725 at the 95 % confidence level. Results of the statistical analysis are given in table 3.

8.2.2.4 Three laboratories were rejected as Cochran outliers; two for sample 1 and one for sample 4.

9 Test report

The test report shall include the following information:

a) the reference to the method used;

b) the results of the analysis;

c) the number of independent replications;

d) any unusual features noted during the analysis;

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

Table 3 — Results of statistical analysis

Sample reference	Mean g/t	Within-laboratory standard deviation	Between-laboratory standard deviation	Repeatability	Reproducibility
1	4,5	0,0	1,17	0,0	3,32
2	21,3	1,08	1,45	3,06	5,12
3	31,3	0,67	1,98	1,89	5,90
4	80,6	1,12	1,91	3,16	6,26
BAM 285-1	5,8	0,66	0,97	1,87	3,31
BCS 345	195,4	2,07	3,89	5,85	12,5

Annex A
(informative)

Examples of aluminium alloy blocks

Three examples of aluminium alloy blocks are illustrated in figures A.1, A.2 and A.3.

The dimensions of the holes should be adapted according to the dimensions of the beakers.

Dimensions in millimetres

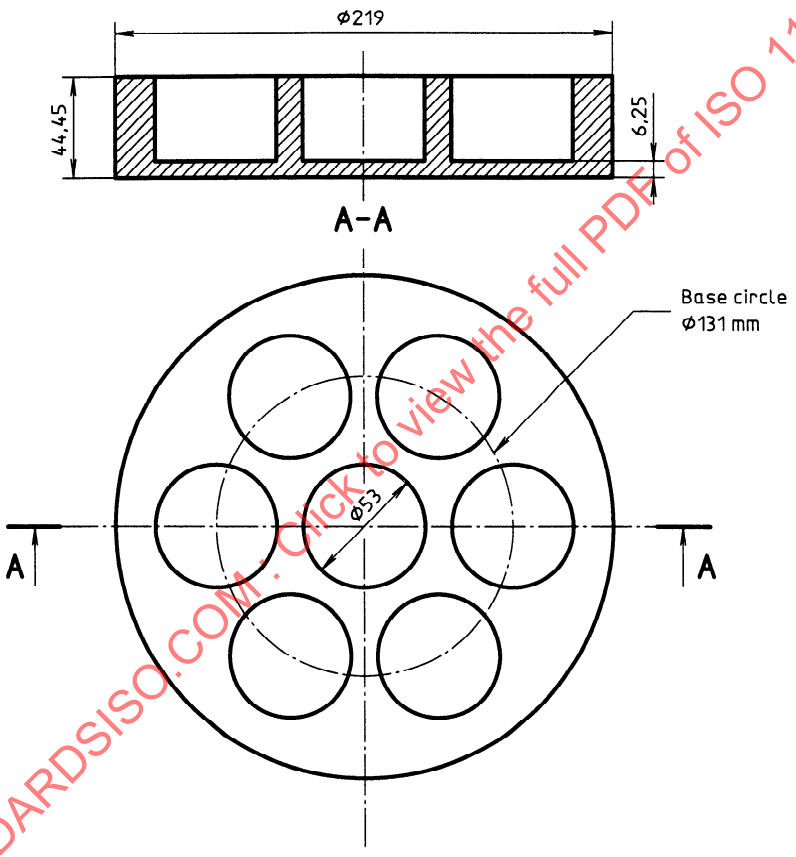

Figure A.1 — Example of an aluminium alloy block 1

Dimensions in millimetres

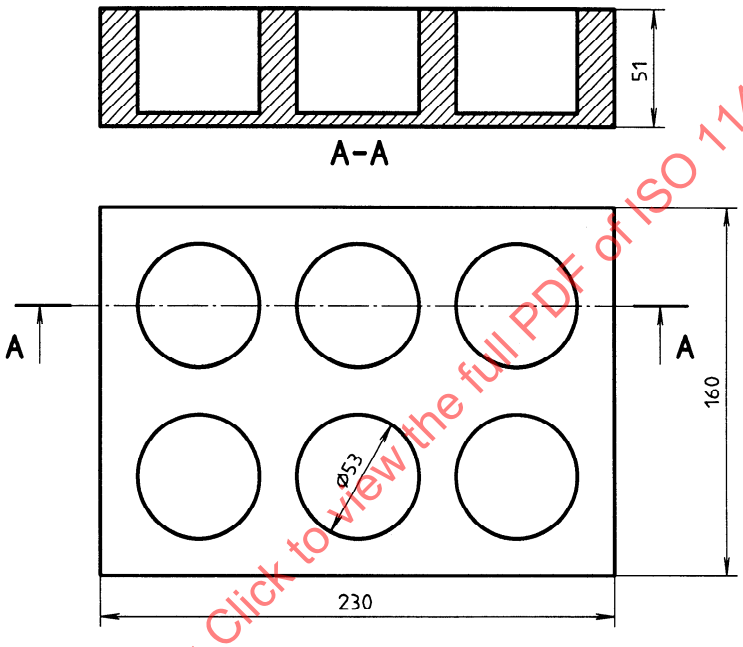

Figure A.2 — Example of an aluminium alloy block 2