
**Steel and iron — Determination of cobalt
content — Flame atomic absorption
spectrometric method**

*Aciers et fontes — Dosage du cobalt — Méthode par spectrométrie
d'absorption atomique dans la flamme*

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Foreword

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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 11652 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

Annex A forms an integral part of this International Standard. Annexes B and C are for information only.

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Printed in Switzerland

Steel and iron – Determination of cobalt content – Flame atomic absorption spectrometric method

1 Scope

This International Standard specifies a flame atomic absorption spectrometric method for the determination of the cobalt content in steel and iron.

The method is applicable to cobalt contents between 0,003 % (*m/m*) and 5,0 % (*m/m*).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were 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 editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements*.

ISO 648:1977, *Laboratory glassware — One-mark pipettes*.¹⁹⁹⁷

ISO 1042:—¹⁾, *Laboratory glassware — One-mark volumetric flasks*.
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ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*.

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*.

ISO 5725-3:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*.

ISO 14284 :1996, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*.

3 Principle

Dissolution of a test portion in hydrochloric, nitric and perchloric acids.

Spraying of the solution into an air-acetylene flame.

Spectrometric measurement of the atomic absorption of the 240,7 nm spectral line emitted by a cobalt hollow cathode lamp.

¹⁾ To be published. (Revision of ISO 1042:1983)

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only grade 2 water as specified in ISO 3696.

4.1 Pure iron, containing less than 0,000 3 % (*m/m*) cobalt.

4.2 Pure nickel, containing less than 0,000 3 % (*m/m*) cobalt.

4.3 Hydrochloric acid, ρ about 1,19 g/ml.

4.4 Nitric acid, ρ about 1,40 g/ml.

4.5 Perchloric acid, ρ about 1,67 g/ml.

4.6 Cobalt, standard solutions.

4.6.1 Standard solution A, corresponding to 1,0 g of Co per litre.

Weigh, to the nearest 0,001 g, 1,000 g of metallic cobalt [purity > 99,9 % (*m/m*) Co]. Transfer to a 250 ml beaker. Add 15 ml of water and 15 ml of nitric acid (4.4). Cover the beaker with a watch-glass, heat gently until complete dissolution has taken place and boil to remove oxides of nitrogen.

Cool to room temperature, transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution A contains 1,0 mg of Co.

4.6.2 Standard solution B, corresponding to 0,2 g of Co per litre.

Transfer 20,0 ml of the standard solution A (4.6.1) to a 100 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution B contains 0,2 mg of Co.

4.6.3 Standard solution C, corresponding to 0,08 g of Co per litre.

Transfer 8,0 ml of the standard solution A (4.6.1) to a 100 ml one-mark volumetric flask, dilute to the mark with water and mix.

Prepare this standard solution C immediately before use.

1 ml of this standard solution C contains 0,08 mg of Co.

5 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042 as appropriate.

Ordinary laboratory apparatus, and

5.1 Atomic absorption spectrometer, equipped with a cobalt hollow cathode lamp and supplied with air and acetylene sufficiently pure to give a steady clear fuel-lean flame, free from water and oil, and free from cobalt.

The atomic absorption spectrometer used will be satisfactory if, after optimization according to 7.3.4, the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and if it meets the precision criteria given in 5.1.1 to 5.1.3.

It is also desirable that the instrument should conform to the additional performance requirements given in 5.1.4.

5.1.1 Minimum precision (see A.1)

Calculate the standard deviation of 10 measurements of the absorbance of the most concentrated calibration solution. The standard deviation shall not exceed 1,5 % of the mean absorbance.

Calculate the standard deviation of 10 measurements of the absorbance of the least concentrated calibration solution (excluding the zero member). The standard deviation shall not exceed 0,5 % of the mean absorbance of the most concentrated calibration solution.

5.1.2 Limit of detection (see A.2)

This is defined as twice the standard deviation of 10 measurements of the absorbance of a solution containing the appropriate element of a concentration level selected to give an absorbance just above that of the zero member.

The limit of detection of cobalt in a matrix similar to the final test solution shall be better than 0,05 µg of Co per millilitre, for wavelength 240,7 nm.

5.1.3 Graph linearity (see A.3)

The slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 times the value of the slope for the bottom 20 % of the concentration range (expressed as a change in absorbance) determined in the same way.

For instruments with automatic calibration using two or more standards, it shall be established prior to the analysis, by obtaining absorbance readings, that the above requirements for graph linearity are fulfilled.

5.1.4 Characteristic concentration (see A.4)

The characteristic concentration of cobalt in a matrix similar to the final test portion solution shall be better than 0,3 µg of Co per millilitre, for wavelength 240,7 nm.

5.2 Ancillary equipment

A strip chart recorder and/or digital readout device is recommended to evaluate the criteria of 5.1.1 to 5.1.3 and for all subsequent measurements.

Scale expansion may be used until the noise observed is greater than the readout error and is always recommended for absorbances below 0,1. If scale expansion has to be used and the instrument does not have the means to read the value of the scale expansion factor, the value can be calculated by measuring the absorbances of a suitable solution with and without scale expansion and simply dividing the signal obtained.

A background corrector equipped with a deuterium hollow cathode lamp is advisable for the analysis of highly alloyed steels, in order to eliminate interference from an FeO molecular absorption band at the cobalt wavelength.

6 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steel and iron.

7 Procedure

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic material in general.

7.1 Test portion

Weigh a test portion according to the presumed cobalt content as follows:

- a) for cobalt contents up to 2,0 % (m/m), a test portion of about 1,0 g, to the nearest 0,001 g;
- b) for cobalt contents from 2,0 % (m/m) to 5,0 % (m/m), a test portion of about 0,50 g, to the nearest 0,000 5 g.

7.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test for each concentration range (see 7.1) using the same quantities of all the reagents, including the pure iron(4.1) but omitting the test portion.

7.3 Determination

7.3.1 Preparation of the test solution

7.3.1.1 Dissolution of the test portion

Transfer the test portion (7.1) to a 250 ml beaker. Add 10 ml of hydrochloric acid (4.3) and 4 ml of nitric acid (4.4) and cover the beaker with a watch-glass. After effervescence ceases, add 10 ml of perchloric acid (4.5) and heat. Heat until dense white fumes of perchloric acid reflux smoothly in the beaker.

Allow to cool, add 30 ml of water and heat gently to dissolve the salts. Cool again and transfer quantitatively to a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Decant the solution through a dry medium-filter paper, to remove any residue or precipitate, for example graphite, silica or tungstic acid, and collect the filtrate in a dry beaker after discarding the first few millilitres.

7.3.1.2 Dilution of the test solution

Depending on the cobalt content expected in the test portion, prepare the test solution in accordance with a), b), c) or d), as follows.

- a) If the expected cobalt content is up to 0,08 % (m/m), use the filtrate (see 7.3.1.1) undiluted.
- b) If the expected cobalt content is between 0,08 % (m/m) and 0,40 % (m/m), dilute the filtrate as follows.

Transfer 20,0 ml of the filtrate to a 100 ml one-mark volumetric flask, dilute to the mark with water and mix (see note 1).

- c) If the expected cobalt content is between 0,40 % (m/m) and 2,0 % (m/m), dilute the filtrate as follows.

Transfer 10,0 ml of the filtrate to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix (see note 1).

- d) If the expected cobalt content is between 2,0 % (m/m) and 5,0 % (m/m), dilute the filtrate as follows.

Transfer 5,0 ml of the filtrate to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix (see note 1).

NOTE 1 If the filtrate(see 7.3.1.1) has to be diluted to give the test solution, dilute the blank (see 7.2) in exactly the same way.

7.3.2 Preparation of the calibration solution

7.3.2.1 Cobalt contents up to 0,08 % (m/m)

Introduce $(1,00 \pm 0,001)$ g of the pure iron (4.1) into a series of six 250 ml beakers. Add 10 ml of hydrochloric acid (4.3) and 5 ml of nitric acid (4.4) to each beaker and cover them with watch-glasses.

After effervescence ceases, cool, then respectively add, using a burette, the volumes of cobalt standard solution C (4.6.3) given in table 1.

Proceed as specified in 7.3.1.1 from "add 10 ml of perchloric acid (4.5) ..." (omitting the filtration step) to item a) in 7.3.1.2.

Table 1 — Calibration solutions, up to 0,08 % (m/m) cobalt content

Volume of cobalt standard solution C (4.6.3) ml	Corresponding concentration of cobalt in the final test solution $\mu\text{g/ml}$	Corresponding percentage of cobalt in the test sample % (m/m)
0 ¹⁾	0	0
2,0	1,6	0,016
4,0	3,2	0,032
6,0	4,8	0,048
8,0	6,4	0,064
10,0	8,0	0,080

1) Zero member

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7.3.2.2 Cobalt contents between 0,08 % (m/m) and 0,40 % (m/m)

Introduce $(1,00 \pm 0,001)$ g of the pure iron (4.1) into a series of six 250 ml beakers. Add 10 ml of hydrochloric acid (4.3) and 5 ml of nitric acid (4.4) to each beaker and cover them with watch-glasses.

After effervescence ceases, cool, then respectively add, using a burette, the volumes of cobalt standard solution B (4.6.2) given in table 2.

Proceed as specified in 7.3.1.1 from "add 10 ml of perchloric acid (4.5) ..." (omitting the filtration step) to item b) in 7.3.1.2.

Table 2 — Calibration solutions, 0,08 % (m/m) up to 0,40 % (m/m) cobalt content

Volume of cobalt standard solution B (4.6.2) ml	Corresponding concentration of cobalt in the final test solution $\mu\text{g/ml}$	Corresponding percentage of cobalt in the test sample % (m/m)
0 ¹⁾	0	0
4,0	1,6	0,080
8,0	3,2	0,160
12,0	4,8	0,240
16,0	6,4	0,320
20,0	8,0	0,400

1) Zero member

7.3.2.3 Cobalt contents between 0,40 % (m/m) and 2,00 % (m/m)

Introduce $(1,00 \pm 0,001)$ g of the pure iron (4.1) into a series of six 250 ml beakers. Add 10 ml of hydrochloric acid (4.3) and 5 ml of nitric acid (4.4) to each beaker and cover them with watch-glasses.

After effervescence ceases, cool, then respectively add, using a burette, the volumes of cobalt standard solution A (4.6.1) given in table 3.

Proceed as specified in 7.3.1.1 from "add 10 ml of perchloric acid (4.5) ..." (omitting the filtration step) to item c) in 7.3.1.2.

Table 3 — Calibration solutions, 0,40 % (m/m) up to 2,00 % (m/m) cobalt content

Volume of cobalt standard solution A (4.6.1) ml	Corresponding concentration of cobalt in the final test solution $\mu\text{g/ml}$	Corresponding percentage of cobalt in the test sample % (m/m)
0 ¹⁾	0	0
4,0	1,6	0,40
8,0	3,2	0,80
12,0	4,8	1,20
16,0	6,4	1,60
20,0	8,0	2,00

1) Zero member

7.3.2.4 Cobalt contents between 2,0 % (m/m) and 5,0 % (m/m)

Introduce $(0,50 \pm 0,0005)$ g of the pure iron (4.1) into a series of six 250 ml beakers. Add 10 ml of hydrochloric acid (4.3) and 5 ml of nitric acid (4.4) to each beaker and cover them with watch-glasses.

After effervescence ceases, cool, then respectively add, using a burette, the volumes of cobalt standard solution A (4.6.1) given in table 4.

Proceed as specified in 7.3.1.1 from "add 10 ml of perchloric acid (4.5) ..." (omitting the filtration step) to item d) in 7.3.1.2.

Table 4 — Calibration solutions, 2,0 % (m/m) up to 5,0 % (m/m) cobalt content

Volume of cobalt standard solution A (4.6.1) ml	Corresponding concentration of cobalt in the final test solution $\mu\text{g/ml}$	Corresponding percentage of cobalt in the test sample % (m/m)
0 ¹⁾	0	0
5,0	1,0	1,00
10,0	2,0	2,00
15,0	3,0	3,00
20,0	4,0	4,00
25,0	5,0	5,00

1) Zero member

7.3.3 Adjustment of atomic absorption spectrometer

Use the characteristics and settings given in table 5.

Table 5 — Spectrometer characteristics

Element	Characteristic
Type of lamp	Cobalt hollow cathode lamp
Wavelength	240,7 nm
Flame	Air-acetylene fuel-lean flame, adjusted for maximum response
Lamp current	Follow manufacturer's recommendations
Bandwidth	Follow manufacturer's recommendations

WARNING - The manufacturer's recommendations shall be closely followed and particular attention is drawn to the following safety points:

- the explosive nature of acetylene, and regulations concerning its use;
- the need to shield the eyes of the operator from ultraviolet radiation by means of tinted glass;
- the need to keep the burner head clear of deposits because a badly clogged burner may cause a flashback;
- the need to ensure that the liquid trap is filled with water;
- the need always to spray water between the test solutions, blank solution and/or calibration solutions.

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7.3.4 Optimizing the atomic absorption spectrometer settings

Follow the manufacturer's instructions for preparing the instrument for use.
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Adjust the lamp current, the wavelength and the gas flow. Light the burner and spray water until the indication has stabilized.

Set the absorbance value at zero, using water.

Choose a damping setting, or integration time, to give a signal steady enough to fulfil the precision criteria given in 5.1.1 to 5.1.3.

Adjust the flame to be fuel-lean and the burner height to about 1 cm below the light path. Spray alternately the calibration solutions of highest concentration and zero concentration, adjusting the gas flow and burner position (horizontally, vertically and rotationally), until the difference in absorbance between the two solutions is at a maximum. Check that the spectrometer is set accurately on the required wavelength.

The presence of alloying elements, particularly nickel and chromium, may cause chemical interference in the flame. In order to avoid this interference, adjust the flame conditions in accordance with the preliminary test results. The procedure for the preliminary test is as follows.

Prepare a second series of calibration solutions containing up to 0,08 % (*m/m*) cobalt in the same way as in 7.3.2.1, but using 0,700 g of the pure iron (4.1) and 0,300 g of the pure nickel (4.2), instead of (1,00 ± 0,001)g of pure iron.

Record the flow rate for each cobalt content in which the same absorbance is obtained and calculate the average flow rate. This flow rate should be used when making spectrometric measurements.

Evaluate the criteria of 5.1.1 to 5.1.3 and the additional performance requirement of 5.1.4 to ensure that the instrument is suitable for the determination.

7.3.5 Spectrometric measurements

Set the scale expansion so that the calibration solution of highest concentration gives nearly full scale deflection. After the instrument has achieved stability in accordance with the precision criteria given in 5.1.1, select two calibration solutions, one having an absorbance just lower than the test portion solution and one just higher. Spray these first in ascending order, then in descending order, with the test solution as the middle solution, in each case measuring the absorption in relation to water. Spray the complete range of calibration solutions including the zero member, again in ascending and descending order. The means of the last ascending and descending series of calibration solutions are used for the calibration graph.

It is recognized that these procedures cannot be followed with automatic instruments which accept two calibration solutions only. In this case, it is suggested that the two "sandwiching" solutions should not be used for the primary calibration, but should be analysed alternately with the test solution.

Spray calibration solutions at frequent intervals during the measurement of a batch of test-solution determinations. Clean the burner if the results show loss of precision caused by clogging.

Obtain the mean absorbance of each calibration solution.

Obtain the mean absorbance of the test solution and the mean absorbance of the blank test.

NOTE 2 At the conclusion of measurement, spray water to remove traces of perchlorates (see WARNING of clause 7).

7.4 Plotting the calibration graph

It is necessary to prepare a new calibration graph for each series of determinations, and for the range of cobalt contents expected.

If the zero member has a significant absorbance, a more complicated procedure is required. In this case, the concentration of cobalt $\rho_{Co,z}$ in the zero member is calculated using the equation

$$\rho_{Co,z} = \rho_{Co,C1} \times \frac{A_z}{A_{Co,C1} - A_z}$$

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where

$\rho_{Co,C1}$ is the concentration of cobalt, expressed in micrograms per millilitre, added to the first calibration solution;

A_z is the absorbance of the zero member;

$A_{Co,C1}$ is the absorbance of the first calibration solution.

The calculated value $\rho_{Co,z}$ is then added to each of the nominal calibration concentrations in order to obtain a mean calibration graph passing through the origin.

Prepare a calibration graph by plotting the mean absorbance values of the calibration solutions against cobalt content, expressed in micrograms per millilitre.

8 Expression of results

8.1 Method of calculation

Convert the absorbances of the test solution and of the blank test solution to micrograms of cobalt per millilitre by means of the calibration graph (7.4).

The cobalt content, w_{Co} , expressed as a percentage by mass, is given by the equation

$$w_{\text{Co}} = \frac{(\rho_{\text{Co},1} - \rho_{\text{Co},0}) \times D \times 100}{10^6} \times \frac{100}{m} = \frac{(\rho_{\text{Co},1} - \rho_{\text{Co},0}) \times D}{10^2 \times m}$$

where

- $\rho_{\text{Co},0}$ is the concentration, expressed in micrograms per millilitre, of cobalt in the blank test (see 7.2);
- $\rho_{\text{Co},1}$ is the concentration, expressed in micrograms per millilitre, of cobalt in the test solution (see 7.3.1);
- D is the dilution factor [i.e. 1 for 7.3.1.2 a); 5 for 7.3.1.2 b); 25 for 7.3.3.2 c) or 50 for 7.3.1.2 d)];
- m is the mass, in grams, of the test portion.

8.2 Precision

A planned trial of this method was carried out by 13 laboratories, using 13 levels of cobalt contents, each laboratory making three determinations of cobalt content at each level (see notes 3 and 4).

NOTES

- 3 Two of the three determinations were carried out 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.
- 4 The third determination was carried out at a different time (on a different day) by the same operator as in note 3, using the same apparatus with a new calibration.

The details of the test samples used and the mean results obtained are given in tables B.1 and B.2.

The results obtained were treated statistically in accordance with ISO 5725, Parts 1, 2 and 3.

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The data obtained showed a logarithmic relationship between the cobalt content and the repeatability limit (r) and reproducibility limits (R and R_w) of the test results (see note 5), as summarized in table 6. The graphical representation of the data is shown in figure C.1.

NOTE 5 — From the two values obtained on day 1, the repeatability limit (r) and reproducibility limit (R) were calculated using the procedure specified in ISO 5725-2. From the first value obtained on day 1 and the value obtained on day 2, the within-laboratory reproducibility limit (R_w) was calculated using the procedure specified in ISO 5725-3.

Table 6 — Results for repeatability limit and reproducibility limits

Cobalt content % (m/m)	Repeatability limit r	Reproducibility limits	
		R	R_w
0,003	0,000 19	0,000 58	0,000 43
0,005	0,000 28	0,000 87	0,000 65
0,010	0,000 50	0,001 5	0,001 1
0,020	0,000 88	0,002 6	0,001 9
0,050	0,001 9	0,005 4	0,004 0
0,100	0,003 3	0,009 3	0,006 9
0,200	0,005 8	0,016	0,012
0,500	0,012	0,033	0,024
1,00	0,022	0,057	0,042
2,00	0,038	0,099	0,073
5,00	0,081	0,204	0,150