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

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

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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 10138 was prepared by Technical Committee ISO/TC 17, *Steel*.

The publication of this International Standard gives rise to the cancellation of ISO 4936:1984.

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

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

1 Scope

This International Standard specifies a flame atomic absorption spectrometric method for the determination of chromium in non-alloy and low-alloy steels and iron.

The method is applicable to chromium contents between 0,002 % (*m*/*m*) and 2,0 % (*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 377-2:1989, *Selection and preparation of samples and test pieces of wrought steels — Part 2: Samples for the determination of the chemical composition.*

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

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

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

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 acid, followed by oxidation with nitric acid.

Filtration and ignition of the acid insoluble residue. Removal of silica with hydrofluoric acid.

Fusion of the residue with potassium hydrogen sulfate, extraction of the melt in acid and addition of the extract to the reserved filtrate.

Spraying the solution into a dinitrogen monoxide-acetylene flame.

Spectrometric measurement of the atomic absorption of the 357,9 nm or 425,4 nm spectral line emitted by a chromium hollow cathode lamp.

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 2 % (*m*/*m*) chromium.

4.2 Potassium hydrogen sulfate ($KHSO_4$).

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

4.4 Nitric acid, ρ about 1,40 g/ml.

4.5 Hydrofluoric acid, ρ about 1,15 g/ml.

4.6 Sulfuric acid, ρ about 1,84 g/ml.

4.7 Sulfuric acid, ρ about 1,84 g/ml, diluted 1 + 3.

4.8 Background solution.

Weigh, to the nearest 0,01 g, 10,00 g of the pure iron (4.1) into a 1 litre beaker. Add 10 g of potassium hydrogen sulfate (4.2) and 150 ml of hydrochloric acid (4.3). Heat gently until dissolved, then oxidize with 30 ml of nitric acid (4.4) added in small portions. Allow to cool, transfer to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

25 ml of this background solution contains 1,000 g of Fe.

4.9 Chromium, standard solutions.

4.9.1 Stock solution, corresponding to 1,0 g of Cr per litre.

Weigh, to the nearest 0,001 g, 1,000 g of metallic chromium [purity > 99,9 % (*m*/*m*) Cr]. Place in a 250 ml beaker, add 40 ml of hydrochloric acid (4.3), cover the beaker with a watch-glass and dissolve by heating. 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 stock solution contains 1,0 mg of Cr.

4.9.2 Standard solution A, corresponding to 400 mg of Cr per litre.

Transfer 100,0 ml of the stock solution (4.9.1) to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

Prepare this standard solution immediately before use.

1 ml of this standard solution contains 400 µg of Cr.

4.9.3 Standard solution B, corresponding to 100 mg of Cr per litre.

Transfer 10,0 ml of the stock solution (4.9.1) into a 100 ml one-mark volumetric flask, dilute to the mark with water and mix.

Prepare this standard solution immediately before use.

1 ml of this standard solution contains 100 µg of Cr.

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 Platinum crucible, of capacity 30 ml.

5.2 Atomic absorption spectrometer.

A chromium hollow cathode lamp; supplies of dinitrogen monoxide and acetylene sufficiently pure to give a steady clear fuel-lean flame, free from water and oil, and free from chromium.

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 5.2.1 to 5.2.3.

It is also desirable that the instrument should conform to the additional performance requirements given in 5.2.4.

5.2.1 Minimum precision (see clause 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.

5.2.2 Limit of detection (see clause 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 chromium in a matrix similar to the final test portion solution shall be better than 0,05 µg of Cr per millilitre for wavelength 357,9 nm and better than 0,15 µg of Cr per millilitre for wavelength 425,4 nm.

5.2.3 Graph linearity (see clause 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.

5.2.4 Characteristic concentration (see clause A.4).

The characteristic concentration for chromium in a matrix similar to the final test portion solution shall be better than 0,2 µg of Cr per millilitre for wavelength 357,9 nm and better than 0,5 µg of Cr per millilitre for wavelength 425,4 nm.

5.3 Ancillary equipment.

A strip chart recorder and/or digital readout device is recommended to evaluate the criteria of 5.2.1 to 5.2.3 and for all subsequent measurements.

Scale expansion can 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 a suitable solution with and without scale expansion and simply dividing the signal obtained.

6 Sampling

Carry out sampling in accordance with ISO 377 or appropriate national standards for steel and iron.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,001 g, approximately 1,000 g of the test sample.

7.2 Blank test

Parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all the reagents including the pure iron (4.1).

7.3 Determination

7.3.1 Preparation of the test solution

7.3.1.1 Dissolution of the test portion

Place the test portion (7.1) in a 250 ml beaker. Add 15 ml of hydrochloric acid (4.3), cover the beaker with a watch-glass and heat gently until solvent action ceases. Oxidize with 3 ml of nitric acid (4.4) added dropwise and boil for 1 min to remove oxides of nitrogen.

Allow to cool, add about 15 ml of water, filter through a close texture filter paper and collect the filtrate in a 250 ml beaker. Wash the filter paper several times with warm water collecting the washings in the beaker. Reserve the filtrate as the main solution.

7.3.1.2 Treatment of insoluble residue

Transfer the filter paper and residue to a platinum crucible (5.1), dry and ignite at as low a temperature as possible until all carbonaceous matter is removed and finally at about 800 °C for at least 15 min. Cool, add 2 drops of sulfuric acid (4.7) and about 2 ml of hydrofluoric acid (4.5). Evaporate to dryness, heat to about 800 °C and cool. Add 1 g of potassium hydrogen sulfate (4.2) and fuse carefully until a clear melt is obtained.

For residues which contained chromium carbide, prolonged heating may be necessary for complete fusion. The potassium hydrogen sulfate can be regenerated by allowing the melt to cool, adding 2 drops of sulfuric acid (4.6) and repeating the fusion until the residue has dissolved.

After cooling, add 10 ml of water and 2 ml of hydrochloric acid (4.3) to the solidified melt in the crucible, transfer the contents to a 250 ml beaker and heat gently until the solid has dissolved. Cool and add the extract to the main solution (see 7.3.1.1).

7.3.1.3 Dilution of the test solution

According to the expected chromium content, dilute the test solution (see 7.3.1.2) to the following volume:

a) for chromium contents up to 0,1 % (*m*/*m*), exactly 100 ml;

b) for chromium contents between 0,1 % (*m*/*m*) and 2,0 % (*m*/*m*), exactly 500 ml.

7.3.2 Preparation of the calibration solutions

According to the chromium content, prepare the calibration solutions by the following procedures.

a) For chromium contents up to 0,1 % (*m*/*m*), introduce 25,0 ml of background solution (4.8) into a series of seven 100 ml one-mark volumetric flasks, then respectively add, using a pipette or burette, the volumes of chromium standard solution B (4.9.3) indicated in table 1. Dilute to the mark with water and mix.

Table 1

Volume of chromium standard solution B (4.9.3) ml	Corresponding mass of chromium mg
0[1]	0
1,0	0,1
2,0	0,2
4,0	0,4
6,0	0,6
8,0	0,8
10,0	1,0

[1] Zero member.

b) For chromium contents between 0,1 % (*m*/*m*) and 0,5 % (*m*/*m*), introduce 5,0 ml of background solution (4.8) into a series of seven 100 ml one-mark volumetric flasks, then respectively add, using a pipette or burette, the volumes of chromium standard solution B (4.9.3) indicated in table 1. Dilute to the mark with water and mix.

c) For chromium contents between 0,5 % (*m*/*m*) and 2,0 % (*m*/*m*), introduce 5,0 ml of background solution (4.8) into a series of seven 100 ml one-mark volumetric flasks, then respectively add, using a pipette or burette, the volumes of chromium standard solution A (4.9.2) indicated in table 2. Dilute to the mark with water and mix.

Table 2

Volume of chromium standard solution A (4.9.2) ml	Corresponding mass of chromium mg
0[1]	0
1,0	0,4
2,0	0,8
4,0	1,6
6,0	2,4
8,0	3,2
10,0	4,0

[1] Zero member.

7.3.3 Adjustment of atomic absorption spectrometer

See table 3.

Table 3

Element	Characteristic
Type of lamp	Chromium hollow cathode
Wavelength	Chromium contents up to 0,5 % (*m*/*m*): 357,9 nm Chromium contents greater than 0,5 % (*m*/*m*): 425,4 nm
Flame	Dinitrogen monoxide-acetylene fuel-lean flame adjusted for maximum chromium response
Lamp current	Follow manufacturer's recommendations
Bandwith	Follow manufacturer's recommendations

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

a) the explosive nature of acetylene, and regulations concerning its use;

b) the need to shield the eyes of the operator from ultraviolet radiation by means of tinted glass;

c) the need to keep the burner head clear of deposits because a badly clogged burner may cause a flashback;

d) the need to ensure that the liquid trap is filled with water;

e) always spray water between the test solutions, blank solution and/or calibration solutions.

In the absence of bandwidth recommendations from the manufacturer (as mentioned in table 3) the following guideline is suggested:

Chromium 357,9 nm — bandwidth between 0,2 nm and 1,0 nm

Chromium 425,4 nm — bandwidth between 0,2 nm and 1,0 nm

7.3.4 Optimizing the atomic absorption spectrometer settings

Follow the manufacturer's instructions for preparing the instrument for use.

When the current to the lamp, the wavelength and the flow of gas have been adjusted and the burner lit, 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 5.2.1 to 5.2.3.

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

Evaluate the criteria of 5.2.1 to 5.2.3 and the additional performance requirement of 5.2.4 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 5.2.1, 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.

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 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.

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 chromium contents expected.

Usually the zero member has a negligibly small absorbance but if the zero member has a significant absorbance a more complicated procedure is required. In this case, the concentration of chromium $\rho_{\mathrm{Cr,z}}$ in the zero member can be calculated using the equation

$$\rho_{\mathrm{Cr,z}} = \rho_{\mathrm{Cr,c1}} \times \frac{A_{\mathrm{z}}}{A_{\mathrm{c1}} - A_{\mathrm{z}}}$$

where

$\rho_{\mathrm{Cr,c1}}$ is the concentration of chromium, expressed in micrograms per millilitre, added to the first calibration solution;

A_{z} is the absorbance of the zero member;

A_{c1} is the absorbance of the first calibration solution.

The derived value $\rho_{\mathrm{Cr,z}}$ 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 chromium content, expressed in micrograms per millilitre. Refer the absorbances of the two adjacent calibration solutions to the graph. If these two calibration readings do not deviate from the graph by more than the permitted precision criteria then the test solution readings are also acceptable.

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 Cr per millilitre by means of the calibration graph (7.4).

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

$$w_{\mathrm{Cr}} = \frac{(\rho_{\mathrm{Cr,1}} - \rho_{\mathrm{Cr,0}}) \times \frac{V}{100} \times 100}{10^6} \times \frac{100}{m}$$

$$= \frac{(\rho_{\mathrm{Cr,1}} - \rho_{\mathrm{Cr,0}}) \times V}{10^4 m}$$

where

$\rho_{\mathrm{Cr,0}}$ is the concentration, expressed in micrograms per millilitre of chromium in the blank test (7.2);

$\rho_{Cr,1}$ is the concentration, expressed in micrograms per millilitre, of chromium in the test solution derived from the calibration graph (7.4);

V is the volume, in millilitres, of the diluted test solution (7.3.1.3);

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

8.2 Precision

A planned trial of this method was carried out by 19 laboratories, at eight levels of chromium, each laboratory making three determinations (see notes 1 and 2) of chromium at each level.

The test samples used are listed in annex B.

The results obtained were treated statistically in accordance with ISO 5725.

The data obtained showed a logarithmic relationship between chromium content and repeatability (r) and reproducibility (R and R_w) of the test results (see note 3) as summarized in table 4. The graphical representation of the figures is given in annex C.

Table 4

Chromium content	Repeatability	Reproducibility	
% (m/m)	r	R	R_w
0,002	0,000 30	0,000 74	0,000 44
0,005	0,000 53	0,001 31	0,000 81
0,01	0,000 83	0,002 03	0,001 28
0,02	0,001 30	0,003 15	0,002 03
0,05	0,002 35	0,005 62	0,003 75
0,1	0,003 66	0,008 70	0,005 96
0,2	0,005 72	0,013 5	0,009 47
0,5	0,010 3	0,024 0	0,017 5
1,0	0,016 1	0,037 2	0,027 8
2,0	0,025 1	0,057 6	0,044 1

NOTES

1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725, i.e. one operator, same apparatus, identical operating conditions, same calibration, and a minimum period of time.

2 The third determination was carried out a different time (on a different day) by the same operator as in note 1 above using the same apparatus with a new calibration.

3 From the results obtained on day 1 the repeatability (r) and reproducibility (R) were calculated using the procedure specified in ISO 5725. From the first result obtained on day 1 and the result obtained on day 2, the within-laboratory reproducibility (R_w) was calculated.

9 Test report

The test report shall include the following information:

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

b) the method used by reference to this International Standard;

c) the results, and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this International Standard, or any optional operation which may have influenced the results.

Annex A
(normative)

Procedures for the determination of instrumental criteria

For the preparation of standard methods of analysis using flame atomic absorption spectrometry, the values below should be decided from interlaboratory test results, by the working group in charge.

A.1 Determination of minimum precision

Spray the most concentrated calibration solution 10 times to obtain 10 individual absorbance readings $A_{\mathrm{A}i}$ and calculate the mean value $\bar{A}_{\mathrm{A}}$.

Spray the least concentrated calibration solution (excluding the zero member) 10 times to obtain 10 individual absorbance readings $A_{\mathrm{B}i}$ and calculate the mean value $\bar{A}_{\mathrm{B}}$.

The standard deviations s_{A} and s_{B} of the absorbance readings of the most and the least concentrated calibration solutions respectively are obtained from

$$s_{\mathrm{A}} = \sqrt{\frac{\Sigma(A_{\mathrm{A}i} - \bar{A}_{\mathrm{A}})^2}{9}}$$

$$s_{\mathrm{B}} = \sqrt{\frac{\Sigma(A_{\mathrm{B}i} - \bar{A}_{\mathrm{B}})^2}{9}}$$

The minimum precisions of the most and least concentrated calibration solutions are obtained from $s_{\mathrm{A}} \times 100/\bar{A}_{\mathrm{A}}$ and $s_{\mathrm{B}} \times 100/\bar{A}_{\mathrm{A}}$ respectively.

A.2 Determination of limit of detection $\rho_{\mathrm{Cr,\,min}}$

Prepare two solutions each containing the same matrix concentration as the sample solution, but with the element of interest at the following known concentrations:

— ρ'_{Cr} µg/ml to give an absorbance A' of approximately 0,01;

— matrix blank to give an absorbance A_0.

Spray the ρ'_{Cr} solution and blank solution 10 times, each recording each reading for about 10 s, and using sufficient scale expansion to make the fluctuations in signal clearly visible.

Obtain the mean absorbance readings $\bar{A}'$ and $\bar{A}_0$.

The standard deviation $s_{A'}$ is given by the equation

$$s_{A'} = \sqrt{\frac{\Sigma(A'_i - \bar{A}')^2}{9}}$$

where

A'_i is the individual measured absorbance reading;

$\bar{A}'$ is the mean value of A'_i.

The limit of detection $\rho_{\mathrm{Cr,min}}$ is given by

$$\rho_{\mathrm{Cr,min}} = \frac{\rho'_{\mathrm{Cr}} \times s_{A'} \times k}{\bar{A}' - \bar{A}_0}$$

(k is normally taken as 2)

A.3 Criterion for graph linearity

Having established the calibration graph, before the application of any curve-straightening device, obtain the net absorbance value A_{A} corresponding to the top 20 % of the concentration range and the net absorbance A_{B} corresponding to the bottom 20 % of the concentration range. Calculate $A_{\mathrm{A}}/A_{\mathrm{B}}$. This must not be less than 0,7. (See figure A.1.)

A.4 Determination of characteristic concentration $\rho_{\mathrm{Cr,k}}$

Prepare a solution containing the same matrix concentration as the sample solution, but with the element of interest at the following known concentration:

— ρ_{Cr} µg/ml to give an absorbance A of approximately 0,1.

Spray the ρ_{Cr} solution and the blank solution without scale expansion and measure the absorbances A and A_0. The characteristic concentration $\rho_{\mathrm{Cr,k}}$ is given by

$$\rho_{\mathrm{Cr,k}} = \frac{\rho_{\mathrm{Cr}} \times 0{,}004\,4}{A - A_0}$$