TECHNICAL
REPORT

ISO/TR 9769

Fourth edition
2018-12

Steel and iron — Review of available methods of analysis

Aciers et fontes — Vue d'ensemble des méthodes d'analyse disponibles

Reference number
ISO/TR 9769:2018(E)

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Published in Switzerland

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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 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

This fourth edition cancels and replaces the third edition (ISO/TR 9769:1991), which has been technically revised to update all the standard methods for the determination of chemical composition of steel and iron.

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.

Steel and iron — Review of available methods of analysis

1 Scope

This document gives guidelines for the determination of the chemical composition of steel and iron by reference to published International Standards, including their range of application and principles of the methods.

Graphical representation of the precision data precision data for the methods is given in Annex A.

The list of International Standards is summarized in Annex B.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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/

3.1
routine method
method calibrated against reference materials, certified reference materials or against standard solutions commercially available that is widely used for control purposes (day-to-day analysis)

4 International Standards for determining the chemical composition of steel and iron, their range of application and principles of the methods

4.1 Mono-elemental methods

4.1.1 Aluminium, Al

Document: ISO 9658:1990, *Steel — Determination of aluminium content — Flame atomic absorption spectrometric method*.

Range of application:

— determination of acid-soluble and/or total aluminium contents between a mass fraction of 0,005 % and a mass fraction of 0,20 % in non-alloyed steel.

Principle of the method:

a) dissolution of a test portion in dilute hydrochloric and nitric acids;

b) fusion of the acid-insoluble material with a mixture of orthoboric acid and potassium carbonate;

c) spraying of the solution into a dinitrogen monoxide-acetylene flame;

d) spectrometric measurement of the atomic absorption of the 309,3 nm spectral line emitted by an aluminium hollow cathode lamp.

4.1.2 Antimony, Sb

Document: ISO 10698:1994, *Steel — Determination of antimony content — Electrothermal atomic absorption spectrometric method*.

Range of application:

— determination of the antimony content between a mass fraction of 0,000 5 % and a mass fraction of 0,010 % in steel.

Principle of the method:

a) dissolution of a test portion in hydrochloric and nitric acids and dilution of the solution to a known volume;

b) introduction of a known volume of the solution into an electrothermal atomizer of an atomic absorption spectrometer;

c) measurement of the atomic absorption of the 217,6 nm spectral resonance line energy emitted by an antimony lamp, using background correction;

d) calibration by the standard additions technique.

4.1.3 Arsenic, As

Document: ISO 17058:2004, *Steel and iron — Determination of arsenic content — Spectrophotometric method*.

Range of application:

— determination of the arsenic content between 0,000 5 % (mass fraction) and 0,10 % (mass fraction) in steel and iron.

Principle of the method:

a) dissolution of a test portion in a hydrochloric acid and nitric acid mixture;

b) prolonged heating with sulfuric acid until white fumes are given off;

c) reduction of arsenic in the presence of hydrazine sulfate and potassium bromide, then separation by distillation as the trivalent chloride, absorbed in the nitric acid solution, in which the As(III) is oxidized back to the pentavalent state As(V);

d) formation of the molybdenum blue complex between ammonium molybdate and arsenic, which is reduced by hydrazine sulfate;

e) spectrophotometric measurement at a wavelength of approximately 840 nm.

4.1.4 Boron, B

4.1.4.1 Document: ISO 10153:1997, *Steel — Determination of boron content — Curcumin spectrophotometric method*.

Range of application:

— determination of the boron content between a mass fraction of 0,000 1 % and a mass fraction of 0,000 5 % only in unalloyed steel, and between a mass fraction of 0,000 5 % and a mass fraction of 0,012 % in steel.

Principle of the method:

a) dissolution of a test portion in hydrochloric and nitric acids;

b) decomposition of boron compounds (nitrides etc.) with orthophosphoric and sulfuric acids at a temperature of 290 °C;

c) formation of a coloured complex between orthoboric acid and curcumin in a buffered acetic medium;

d) spectrophotometric measurement at a wavelength of about 543 nm.

4.1.4.2 Document: ISO 13900:1997, *Steel — Determination of boron content — Curcumin spectrophotometric method after distillation*.

Range of application:

— determination of the boron content between a mass fraction of 0,000 05 % and a mass fraction of 0,001 0 % in steel.

Principle of the method:

a) dissolution of a test portion in hydrochloric and nitric acids;

b) decomposition of boron compounds (nitrides etc.) with orthophosphoric and sulfuric acids at a temperature of 290 °C;

c) distillation of the solution after the addition of methanol and collection of methylborate in a receiver containing sodium hydroxide solution;

d) evaporation of the solution to dryness; formation of a coloured complex between orthoboric acid and curcumin in a methanol medium;

e) spectrophotometric measurement at a wavelength of about 550 nm.

4.1.5 Calcium, Ca

4.1.5.1 Document: ISO 10697-1:1992, *Steel — Determination of calcium content by flame atomic absorption spectrometry — Part 1: Determination of acid-soluble calcium content*.

Range of application:

— determination of acid-soluble calcium content between a mass fraction of 0,000 5 % and a mass fraction of 0,003 % in steel.

Principle of the method:

a) dissolution of a test portion in hydrochloric and nitric acids;

b) addition of potassium chloride/lanthanum nitrate solution as a spectrochemical buffer;

c) spraying of the solution into a dinitrogen monoxide-acetylene flame;

d) spectrometric measurement of the atomic absorption of the 422,7 nm spectral line emitted by a calcium hollow cathode lamp.

4.1.5.2 Document: ISO 10697-2:1994, *Steel — Determination of calcium content by flame atomic absorption spectrometry — Part 2: Determination of total calcium content*.

Range of application:

— determination of the total calcium content between a mass fraction of 0,000 5 % and a mass fraction of 0,005 % in steel.

Principle of the method:

a) dissolution of a test portion in hydrochloric and nitric acids;

b) fusion of the acid-insoluble residue with sodium carbonate;

c) addition of potassium chloride/lanthanum nitrate solution as a spectrochemical buffer;

d) spraying of the solution into a dinitrogen monoxide-acetylene flame;

e) spectrometric measurement of the atomic absorption of the 422,7 nm spectral line emitted by a calcium hollow cathode lamp.

4.1.6 Carbon, C

4.1.6.1 Document: ISO 9556:1989, *Steel and iron — Determination of total carbon content — Infrared absorption method after combustion in an induction furnace*.

Range of application:

— determination of the total carbon content between a mass fraction of 0,003 % and a mass fraction of 4,5 % in steel and iron.

Principle of the method:

a) combustion of a test portion with accelerator at a high temperature in a high-frequency induction furnace in a current of pure oxygen; transformation of carbon into carbon dioxide and/or carbon monoxide;

b) measurement by infrared absorption of the carbon dioxide and/or carbon monoxide carried by a current of oxygen.

4.1.6.2 Document: ISO 15349-2:1999, *Unalloyed steel — Determination of low carbon content — Part 2: Infrared absorption method after combustion in an induction furnace (with preheating)*.

Range of application:

— determination of the carbon contents between a mass fraction of 0,000 3 % and a mass fraction of 0,010 % in unalloyed steel.

Principle of the method:

a) preheating of a test portion at low temperature and combustion of a test portion with accelerator at a high temperature in an induction furnace in a current of pure oxygen; transformation of carbon into carbon dioxide and/or carbon monoxide;

b) measurement of infrared absorption of the carbon dioxide or carbon dioxide/carbon monoxide evolved from steel and carried by a current of pure oxygen;

c) calibration graph is established using sucrose or calcium carbonate.

4.1.6.3 Document: ISO/TS 10719:2016, *Cast irons — Determination of non-combined carbon content — lnfrared absorption method after combustion in an induction furnace*.

Range of application:

— determination of non-combined carbon content between a mass fraction of 1,0 % and a mass fraction of 3,0 % in cast irons.

NOTE Elements ordinarily present do not interfere. However, some alloyed cast irons, when extensively heat treated, contain carbides that are not soluble when using this method and can give high values for non-combined carbon.

Principle of the method:

a) decomposition of a test portion with nitric acid in the presence of methanol and treatment with hydrofluoric acid; removal of the non-combined carbon by filtering through a glass-fibre filter;

b) combustion of the glass-fibre filter containing the non-combined carbon in a flow of oxygen at a high temperature, using a high-frequency induction furnace, in the presence of pure iron and an accelerator; transformation of carbon into carbon dioxide and/or carbon monoxide;

c) measurement by infrared absorption of the carbon dioxide and/or carbon monoxide, carried by the current of oxygen.

4.1.7 Chromium, Cr

4.1.7.1 Document: ISO 4937:1986, *Steel and iron — Determination of chromium content — Potentiometric or visual titration method.*

Range of application:

— determination of chromium contents between a mass fraction of 0,25 % and a mass fraction of 35 % in steel and iron.

NOTE If vanadium is present, the visual titration is applicable only to test portions containing less than 3 mg of vanadium.

Principle of the method:

a) dissolution of a test portion with appropriate acids;

b) oxidation of chromium in an acid medium to chromium(Vl) by ammonium peroxydisulfate in the presence of silver sulfate; reduction of manganese(VII) by hydrochloric acid;

c) reduction of chromium(VI) by ammonium iron(ll) sulfate standard solution;

d) in the case of potentiometric detection, determination of the equivalence point by measurement of the potential variation when the ammonium iron(ll) sulfate standard solution is being added;

e) in the case of visual detection, titration of the excess ammonium iron(ll) sulfate by potassium permanganate standard solution, which also acts as the indicator.

4.1.7.2 Document: ISO 10138:1991, *Steel and iron — Determination of chromium content — Flame atomic absorption spectrometric method*.

Range of application:

— determination of chromium contents between a mass fraction of 0,002 % and a mass fraction of 2,0 % in non-alloy and low-alloy steels and iron.

Principle of the method:

a) dissolution of a test portion in hydrochloric acid, followed by oxidation with nitric acid;

b) filtration and ignition of the acid insoluble residue; removal of silica with hydrofluoric acid;

c) fusion of the residue with potassium hydrogen sulfate, extraction of the melt in acid and addition of the extract to the reserved filtrate;

d) spraying the solution into a dinitrogen monoxide-acetylene flame;

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

4.1.7.3 Document: ISO 15355:1999, *Steel and iron — Determination of chromium content — Indirect titration method*.

Range of application:

— determination of chromium content between a mass fraction of 1 % and a mass fraction of 35 % in steel and iron.

Vanadium contents in steel and iron should be less than a mass fraction of 1 % for chromium contents higher than a mass fraction of 10 % and less than a mass fraction of 0,2 % for chromium contents less than a mass fraction of 10 %.

Principle of the method:

a) fusion of the sample with sodium peroxide followed by acidification with sulfuric acid;

b) oxidization of chromium(III) to dichromate with peroxodisulfate using silver as a catalyst;

c) reduction of the dichromate with an excess of a solid iron(II) salt and potentiometric back titration of the excess with a dichromate solution;

d) any interference from vanadium is corrected mathematically.

4.1.8 Cobalt, Co

4.1.8.1 Document: ISO 11652:1997, *Steel and iron — Determination of cobalt content — Flame atomic absorption spectrometric method*.

Range of application:

— determination of the cobalt content between a mass fraction of 0,003 % and a mass fraction of 5,0 % in steel and iron.

Principle of the method:

a) dissolution of a test portion in hydrochloric, nitric and perchloric acids;

b) spraying of the solution into an air-acetylene flame;

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

4.1.8.2 Document: ISO 11653:1997, *Steel — Determination of high cobalt content — Potentiometric titration method after separation by ion exchange*.

Range of application:

— determination of cobalt content between a mass fraction of 5,0 % and a mass fraction of 17,0 % in steel.

Principle of the method:

a) dissolution of a test portion in a mixture of nitric and hydrochloric acids;

b) separation of cobalt from interfering elements by selective elusion from an anion exchange column using hydrochloric acid;

c) oxidation with perchloric acid; removal of dissolved chlorine and oxygen with a stream of nitrogen;

d) addition of the test solution to a solution containing ammonium citrate, ammonium hydroxide and an excess of potassium hexacyanoferrate(lll) standard solution and titration of the excess with a standard cobalt solution using potentiometric end-point detection.

4.1.8.3 Document: ISO 13898-4:1997, *Steel and iron — Determination of nickel, copper and cobalt contents — Inductively coupled plasma atomic emission spectrometric method — Part 4: Determination of cobalt content*.

Range of application:

— determination of cobalt content between a mass fraction of 0,001 % and a mass fraction of 0,10 % in unalloyed steel and unalloyed iron.

Principle of the method:

a) dissolution of a test portion in a mixture of hydrochloric and nitric acids and dilution of the solution to known volume;

b) if necessary, addition of scandium or yttrium as internal standard;

c) nebulization of the solution into an inductively coupled plasma atomic emission spectrometer (ICP-AES) and measurement of the intensity of the emitted light from each element, or with emitted light from scandium or yttrium, simultaneously; examples of the analytical lines are given in ISO 13898-1:1997, Table 2.

4.1.9 Copper, Cu

4.1.9.1 Document: ISO 4943:1985, *Steel and cast iron — Determination of copper content — Flame atomic absorption spectrometric method*.

Range of application:

— determination of copper contents in the range of a mass fraction of 0,004 % to a mass fraction of 0,5 % in steel and cast iron.

Principle of the method:

a) dissolution of a test portion in a mixture of hydrochloric, nitric and perchloric acids;

b) spraying of the solution into an air-acetylene flame; spectrometric measurement of the atomic absorption of the 324,7 nm spectral line emitted by a copper hollow cathode lamp.

4.1.9.2 Document: ISO 4946:2016, *Steel and cast iron — Determination of copper — 2,2'-Biquinoline spectrophotometric method*.

Range of application:

— determination of copper mass fraction in the range of 0,02 % and 5 % in steel and cast iron.

Principle of the method:

a) dissolution of a test portion in appropriate acids;

b) fuming with perchloric acid to remove hydrochloric and nitric acids and dehydrate silicic acid;

c) reduction of copper(II) to copper(I) in hydrochloric acid solution by means of ascorbic acid; formation of a coloured compound of copper(I) with 2,2′-biquinoline;

d) spectrophotometric measurement at a wavelength of about 545 nm.

4.1.9.3 Document: ISO 13898-3:1997, *Steel and iron — Determination of nickel, copper and cobalt contents — Inductively coupled plasma atomic emission spectrometric method — Part 3: Determination of copper content*.

Range of application:

— determination of copper content between a mass fraction of 0,001 % and a mass fraction of 0,40 % in unalloyed steel and unalloyed iron.

Principle of the method:

a) dissolution of a test portion in a mixture of hydrochloric and nitric acids and dilution of the solution to known volume;

b) if necessary, addition of scandium or yttrium as internal standard;

c) nebulization of the solution into an ICP-AES and measurement of the intensity of the emitted light from each element, or with emitted light from scandium or yttrium, simultaneously; examples of the analytical lines are given in ISO 13898-1:1997, Table 2.

4.1.10 Manganese, Mn

4.1.10.1 Document: ISO 629:1982, *Steel and cast iron — Determination of manganese content — Spectrophotometric method*.

Range of application:

— determination of manganese contents between a mass fraction of 0,001 % and a mass fraction of 4 % in steel and cast iron.

Principle of the method:

a) dissolution of a test portion in sulfuric-phosphoric acid mixture and nitric acid; treatment of the test solution with perchloric acid; formation of the permanganate ion by sodium periodate;

b) spectrophotometric measurement of the test solution at wavelength of about 545 nm.

4.1.10.2 Document: ISO 10700:1994, *Steel and iron — Determination of manganese content — Flame atomic absorption spectrometric method*.

Range of application:

— determination of manganese content between a mass fraction of 0,002 % and a mass fraction of 2,0 % in steel and iron.

Principle of the method:

a) dissolution of a test portion in hydrochloric and nitric acids followed by evaporation with perchloric acid until white fumes appear;

b) spraying of the solution into an air-acetylene flame;

c) spectrometric measurement of the atomic absorption of the 279,5 nm spectral line emitted by a manganese hollow cathode lamp.

4.1.10.3 Document: ISO 10278:1995, *Steel — Determination of manganese content — Inductively coupled plasma atomic emission spectrometric method*.

Range of application:

— determination of the manganese content between a mass fraction of 0,002 % and a mass fraction of 1,5 % in unalloyed steels.

Principle of the method:

a) dissolution of a test portion in a mixture of hydrochloric and nitric acids and dilution of the solution to a known volume;

b) if necessary, addition of scandium or yttrium as an internal standard;

c) nebulization of the solution into an ICP-AES and measurement of the intensity of the emitted light from manganese at 257,61 nm and, optionally, emitted light from scandium at 361,38 nm or yttrium at 371,03 nm, simultaneously.

4.1.10.4 Document: ISO 18632:2018, *Alloyed steels — Determination of manganese — Potentiometric or visual titration method*.

Range of application:

— determination of the mass fraction of manganese between 2 % and 25 % in alloyed steels.

NOTE Vanadium and cerium interfere with the determination. If the mass fraction of cerium in the sample is less than 0,01 %, or the mass fraction of vanadium in the sample is less than 0,005 %, the interference is negligible, otherwise theoretical corrections are necessary.

Principle of the method:

a) dissolution of a test portion in appropriate acids;

b) addition of phosphoric acid; oxidation of manganese to manganese(III) in phosphoric acid medium with ammonium nitrate;

c) visual titration of manganese(III) with ferroammoniumdisulfate standard solution with N-phenylanthranilic acid as the indicator;

d) alternatively, potentiometric titration with ferroammoniumdisulfate standard solution; if the sample contains vanadium and cerium, the mass fraction of manganese is corrected.

4.1.11 Molybdenum, Mo

4.1.11.1 Document: ISO 4941:1994, *Steel and iron — Determination of molybdenum content — Thiocyanate spectrophotometric method*.

Range of application:

— determination of the molybdenum content between a mass fraction of 0,005 % and a mass fraction of 0,125 % in steel and iron.

NOTE 1 Vanadium and tungsten interfere with the measurement if, because of their contents, the V/Mo ratio is greater than 16 or the W/Mo ratio is greater than 8 (see NOTE 2).

NOTE 2 Greater V/Mo or W/Mo ratios (up to 300) can occur, but in such cases it is necessary to carry out the measurement very quickly after the extraction.

Principle of the method:

a) dissolution of a test portion in an appropriate mixture of acids and decomposition of the carbides by oxidation;

b) quantitative formation of a coloured compound of molybdenum, in the presence of thiocyanate, iron(ll) and/or copper(ll) ions and extraction of this compound using butyl acetate;

c) spectrophotometric measurement of the coloured compound at a wavelength of about 470 nm.

4.1.11.2 Document: ISO/TS 13899-1:2004, *Steel — Determination of Mo, Nb and W contents in alloyed steel — Inductively coupled plasma atomic emission spectrometric method — Part 1: Determination of Mo content*.

Range of application:

— determination of molybdenum content between a mass fraction of 0,03 % and a mass fraction of 8,5 % in steel.

Principle of the method:

a) dissolution of a test portion in a mixture of hydrochloric, nitric and phosphoric acid and fuming with a mixture of phosphoric and perchloric acids;

b) addition of hydrofluoric acid and, if necessary, an internal reference element and dilution of the solution to known volume;

c) nebulization of the solution into an ICP-AES and measurement of the intensity of the emitted light from molybdenum, or with emitted light from the internal reference element, simultaneously.

NOTE 1 The method uses a calibration graph based on a very close matrix matching of the calibration solutions to the sample and close bracketing of the contents around the approximate concentration of molybdenum in the sample to be analysed. The concentrations of all elements in the sample have to be, therefore, approximately known. If the concentrations are not known, the sample has to be analysed by some semi-quantitative method.

NOTE 2 The advantage with this procedure is that all possible interferences from the matrix are automatically compensated, which results in high accuracy. This is most important for spectral interferences, which can be severe in very highly alloyed steels. However, all possible interferences have to be kept on a minimum level. Therefore, it is essential that the spectrometer used meets the performance criteria specified in the method for the selected analytical lines.

4.1.12 Nickel, Ni

4.1.12.1 Document: ISO 4940:1985, *Steel and cast iron — Determination of nickel content — Flame atomic absorption spectrometric method*.

Range of application:

— determination of nickel contents in the range of a mass fraction of 0,002 % to a mass fraction of 0,5 % in steel and cast iron.

Principle of the method:

a) dissolution of a test portion in a mixture of appropriate acids followed by evaporation to fuming with perchloric acid;

b) spraying of the solution into an air-acetylene flame; spectrometric measurement of the atomic absorption of the 352,5 nm spectral line emitted by a nickel hollow cathode lamp.

NOTE 1 With some instruments it is not possible to obtain sufficient sensitivity at the wavelength of 352,5 nm for low concentrations of nickel near the bottom end of the application range. In such cases, the alternative wavelength of 232,0 nm is used.