



SWEDISH
STANDARDS
INSTITUTE

SVENSK STANDARD
SS-EN ISO 4934:2004

Fastställd 2004-11-12

Utgåva 1

**Stål och järn – Bestämning av svavelhalt –
Gravimetrisk metod (ISO 4934:2003)**

**Steel and iron – Determination of sulfur content –
Gravimetric method (ISO 4934:2003)**

ICS 77.080.01

Språk: engelska

Publicerad: december 2004

Europastandarden EN ISO 4934:2003 gäller som svensk standard. Detta dokument innehåller den officiella engelska versionen av EN ISO 4934:2003.

Denna standard ersätter SS-EN 24934, utgåva 1.

The European Standard EN ISO 4934:2003 has the status of a Swedish Standard. This document contains the official English version of EN ISO 4934:2003.

This standard supersedes the Swedish Standard SS-EN 24934, edition 1.

Upplysningar om **sakinnehållet** i standarden lämnas av SIS, Swedish Standards Institute, telefon 08 - 555 520 00.

Standarder kan beställas hos SIS Förlag AB som även lämnar **allmänna upplysningar** om svensk och utländsk standard.

Postadress: SIS Förlag AB, 118 80 STOCKHOLM
Telefon: 08 - 555 523 10. *Telefax:* 08 - 555 523 11
E-post: sis.sales@sis.se. *Internet:* www.sis.se

EUROPEAN STANDARD

EN ISO 4934

NORME EUROPÉENNE

EUROPÄISCHE NORM

December 2003

ICS 77.080.01

Supersedes EN 24934:1989

English version

Steel and iron - Determination of sulfur content - Gravimetric method (ISO 4934:2003)

Aciers et fontes - Dosage de soufre - Méthode gravimétrique (ISO 4934:2003)

Stahl und Eisen - Bestimmung des Schwefelgehaltes - Gravimetrisches Verfahren (ISO 4934:2003)

This European Standard was approved by CEN on 10 December 2003.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and United Kingdom.



EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Contents	Page
Foreword	3
1 Scope	4
2 Normative references	4
3 Principle	4
4 Reagents	5
5 Apparatus	6
6 Sampling	7
7 Procedure	7
8 Expression of results	9
9 Test report	10
Annex A (informative) Additional information on international cooperative tests	12
Annex B (informative) Graphical representation of precision data	13
Annex ZA (normative)	14

Foreword

Le présent document (EN ISO 4934:2003) a été élaboré par le Comité Technique ISO/TC 17 "Acier" en collaboration avec le Comité Technique ECISS/TC 20 "Analyses chimiques" dont le secrétariat est tenu par le SIS.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2004, and conflicting national standards shall be withdrawn at the latest by June 2004.

This document supersedes EN 24934:1989.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the United Kingdom.

Endorsement notice

The text of ISO 4934:2003 has been approved by CEN as EN ISO 4934:2003 without any modifications.

NOTE Normative references to International Standards are listed in Annex ZA (normative).

Steel and iron — Determination of sulfur content — Gravimetric method

1 Scope

This International Standard specifies a gravimetric method for the determination of the sulfur content in steels and iron, excluding steels containing selenium. The method is particularly suitable as a reference method for the standardization of samples on which certified standard values are to be established.

The method is applicable to a sulfur content between 0,003 % (mass fraction) and 0,35 % (mass fraction).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 565, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings*

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

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

ISO 5725-2, *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, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*

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

3 Principle

Dissolution of a test portion in dilute nitric acid in the presence of bromine, or in the mixed acid of nitric acid and hydrochloric acid in the presence of bromine (with the aid of an appropriate device to prevent sulfur losses).

Addition of perchloric acid and evaporation of the solution until white fumes of perchloric acid are evolved.

Filtration of the solution and removal of the dehydrates of silicon, tungsten, niobium, etc.

Addition of a determined quantity of sulfate ions to aid precipitation.

Chromatographic separation of the sulfate ions from the test solution by adsorption on an alumina column, and elution using an ammonium hydroxide solution.

Precipitation of the sulfate ions as barium sulfate under controlled conditions and filtering, washing, heating and weighing.

4 Reagents

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

4.1 Aluminium oxide (alumina, Al_2O_3), prepared for chromatography, of particle size corresponding to a sieve mesh size of 75 μm to 150 μm (supplementary series R 40/3 of ISO 565)

Alumina designated alkaline, neutral or acid may be used.

Place approximately 200 g of the dry alumina in a 400 ml beaker containing 300 ml of water and place the beaker in a sink. Insert a glass tube having a bore of 5 mm, such that it extends to the bottom of the beaker and connect the tube to a water supply. Adjust the water flow so that the suspended fine material overflows the rim of the beaker. Continue this treatment until all the fine material, which does not settle within 1 min of stopping the water flow, is removed.

Pour off the supernatant liquid from the coarser material, add the hydrochloric acid (4.5) in an amount sufficient to cover the alumina; stir and allow to stand for not less than 12 h. Pour off the hydrochloric acid and wash the alumina with water as described in the second paragraph.

For preparation of the column, make a slurry of the washed alumina and the hydrochloric acid solution (4.8).

4.2 Bromine (Br_2), min 99 % (mass fraction)

4.3 Nitric acid (HNO_3), ρ = approximately 1,40 g/ml

4.4 Nitric acid (HNO_3), ρ = approximately 1,40 g/ml, diluted 1 + 1

4.5 Hydrochloric acid (HCl), ρ = approximately 1,19 g/ml

4.6 Hydrochloric acid (HCl), ρ = approximately 1,19 g/ml, diluted 1 + 1

4.7 Hydrochloric acid (HCl), ρ = approximately 1,19 g/ml, diluted 1 + 9

4.8 Hydrochloric acid (HCl), ρ = approximately 1,19 g/ml, diluted 1 + 19

4.9 Perchloric acid (HClO_4), ρ = approximately 1,54 g/ml

NOTE If this reagent is shown to have a high sulfate content, this may be removed by passing the reagent through the adsorption column (5.4).

4.10 Perchloric acid (HClO_4), ρ = approximately 1,54 g/ml, diluted 1 + 49

4.11 Acid mixture

Mix hydrochloric acid (4.5) and nitric acid (4.3) in proportions liable to ensure total solubility of the samples. This mixture should be freshly prepared as required.

NOTE Generally, aqua regia can be used. For some samples, the proportion of hydrochloric acid and nitric acid can be adjusted.

4.12 Ammonium hydroxide (NH_4OH), ρ = approximately 0,90 g/ml

4.13 Ammonium hydroxide (NH_4OH), ρ = approximately 0,90 g/ml, diluted 1 + 19

4.14 Ammonium hydroxide (NH_4OH), ρ = approximately 0,90 g/ml, diluted 1 + 99

4.15 Sulfuric acid (H_2SO_4), solution corresponding to approximately 48 mg/l of sulfur

Add 2,8 ml of sulfuric acid, $\rho =$ approximately 1,84 g/ml, to about 500 ml of water. Dilute to 1 000 ml and mix. Take 30 ml of this solution, dilute to 1 000 ml and mix.

4.16 Barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), 1,22 g/l solution

Dissolve 1,22 g of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water, dilute to 1 000 ml and mix. Filter the solution through close texture filter paper just before use.

1 ml of this solution is equivalent to approximately 0,16 mg of sulfur.

4.17 Methyl orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$), 0,50 g/l solution

4.18 Glacial acetic acid (CH_3COOH), $\rho =$ approximately 1,05 g/ml

4.19 Hydrogen peroxide (H_2O_2), $\rho =$ approximately 1,10 g/ml

5 Apparatus

Use normal laboratory apparatus.

5.1 Analytical balance, calibrated with nationally or internationally traceable mass, to provide measurement traceability

5.2 Conical flask, of capacity 1 000 ml, having a ground-glass neck

5.3 Allihn condenser, four- or six-bulb type

5.4 Chromatographic adsorption column (see Figure 1)

Prepare the adsorption column as follows.

Fit the column tube into a one-hole rubber bung just below the valve to act as a gasket for fixing the tube in a suction filtration flask. Fit the tube into the suction flask and place a well-packed plug of quartz wool, about 20 mm thick, in the narrow end of the tube. Turn on the valve. Transfer sufficient alumina slurry (4.1) into the tube to make a column 100 mm to 120 mm long. Using the hydrochloric acid solution (4.8), rinse all the alumina particles from the sides of the reservoir into the tube. Insert a plug of quartz wool and press down with a glass rod so that the quartz wool makes contact with the alumina. Compact the plug again if contact is not maintained with the alumina column. Ensure that all alumina particles are removed from the column sides above the top plug.

Pass 20 ml hydrochloric acid (4.8) and then 20 ml of water through the column and follow with 20 ml of the ammonium hydroxide solution (4.13) and then 20 ml of water. Combine the last two eluates and test for absence of aluminium salts by adjusting the pH of solution until faintly ammoniacal. If aluminium hydroxide precipitates on standing, pass 20 ml of the hydrochloric acid solution (4.7) and then 20 ml of water through the column. Repeat the treatment with 20 ml of the ammonium hydroxide solution (4.13) and 20 ml of water, testing the ammoniacal eluates for absence of aluminium salts as before.

If aluminium hydroxide still precipitates, pass some of the hydrochloric acid solution (4.6) through the column for 1 h without suction and then wash with 50 ml of water. Pass 20 ml of the ammonium hydroxide solution (4.13) and 20 ml of water through the column and test the eluates for absence of aluminium salts.

Repeat this sequence of washing until there is no evidence of aluminium salts being eluted from the column. Finally, wash with 30 ml of the hydrochloric acid solution (4.8).

When the tube is not in use, turn the valve off, fill the tube with hydrochloric acid (4.8) and fit a rubber bung to the reservoir.