SLOVENSKI STANDARD
SIST-TP CEN/TR 10362:2015

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Kemijska analiza železovih zlitin - Določevanje selena v jeklih - Elektrotermična atomska absorpcijska spektrometrija

Chemical analysis of ferrous materials - Determination of selenium in steels - Electrothermal atomic absorption spectrometric method

Chemische Analyse der Eisen und Stahlwerkstoffe - Bestimmung des Selengehaltes in Stahl

Analyse chimique des produits ferreux - Détermination du sélénium dans les aciers - Méthode par spéctrométrie d'absorption atomique éléctrothermique

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TECHNICAL REPORT

RAPPORT TECHNIQUE

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English Version

Chemical analysis of ferrous materials - Determination of selenium in steels - Electrothermal atomic absorption spectrometric method

Analyse chimique des produits ferreux - Détermination du sélénium dans les aciers - Méthode par spectrométrie d'absorption atomique électrothermique

Chemische Analyse von Eisenwerkstoffen - Bestimmung von Selen in Stahl - Spektrometrisches Verfahren mit elektrothermischer Atomabsorption

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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CEN/TR 10362:2014 (E)

Contents

Foreword

This document (CEN/TR 10362:2014) has been prepared by Technical Committee ECISS/TC 102 "Methods of chemical analysis for iron and steel", the secretariat of which is held by SIS.

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1 Scope

This Technical Report specifies an electrothermal atomic absorption spectrometric method for the determination of selenium in steels.

The method is applicable to selenium contents between 0,000 4 % (m/m) and 0,02 % (m/m).

2 Normative references

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

EN ISO 648, *Laboratory glassware - Single-volume pipettes (ISO 648)*

EN ISO 1042, *Laboratory glassware - One-mark volumetric flasks (ISO 1042)*

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696)*

3 Principle

Dissolution of a test portion in hydrochloric and nitric acids and dilution of the solution to a known volume.

Introduction of a known volume of the solution into the electrothermal atomizer of an atomic absorption spectrometer.

Measurement of the absorption of the 196,0 nm spectral line energy emitted by a selenium hollow-cathode lamp, using Zeeman effect background correction.

Calibration by the standard addition technique.

4 Reagents

During the analysis, use only reagents of recognised analytical grade and only grade 3 water, as specified in EN ISO 3696.

4.1 Nitric acid, HNO_3 (ρ_{20} = 1,40 g/ml)

4.2 Hydrochloric acid, HCl (ρ_{20} = 1,19 g/ml)

4.3 Matrix modifiers

The matrix modifiers described in 4.3.1 and 4.3.2 are recommended. Each laboratory has to investigate on its own equipment which of them is the most suitable, regarding sensitivity and recovery.

4.3.1 Palladium-nickel modifier

Prepare a palladium solution (1 mg/ml Pd) by dissolving 167 mg of $PdCl_2$ in 100 ml of hot water and 1 ml of nitric acid (4.1).

Prepare a nickel solution (1 mg/ml) by dissolving 1 g of nickel (Ni > 99,999 %) in 20 ml of water, 20 ml of nitric acid (4.1) and 5 ml of hydrochloric acid (4.1). Heat until the metal is dissolved. After cooling, transfer the solution into a 1 l one-mark volumetric flask, dilute to the mark with water and mix well.

Into a 50 ml volumetric flask, mix 35 ml of the 1 mg/ml palladium solution with 15 ml of the 1 mg/ml nickel solution. This solution contains 700 µg/ml Pd and 300 µg/ml Ni.

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4.3.2 Palladium-magnesium modifier

Prepare a $PdCl_2$ solution by dissolving 500 mg of $PdCl_2$ in 100 ml of hot water and 1 ml of nitric acid (4.1).

Prepare a $Mg(NO_3)_2$ solution by dissolving 350 mg of $Mg(NO_3)_2$. $6H_2O$ in 100 ml of water and 1 ml of nitric acid (4.1).

Mix equal volumes of the $PdCl_2$ solution and the $Mg(NO_3)_2$ solution.

4.4 Selenium standard solution, 1 g/l

Weigh , to the nearest 0,001 g, 1 g of high purity selenium [min 99,9 % (mass fraction)], transfer into a 100 ml beaker and cover with a watch glass.

Dissolve it in 35 ml of nitric acid (4.1). Heat to complete dissolution at a temperature just below the boiling point (approximately 150 °C) during at least 30 minutes. After cooling, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this solution contains 1 mg of selenium.

4.5 Selenium standard solution, 0,01 g/l

Transfer 10,0 ml of selenium standard solution (4.4) into a 1 000 ml one-mark volumetric flask. Add 120 ml of hydrochloric acid (4.2) and 40 ml of nitric acid (4.1). Dilute to the mark with water and mix well.

1 ml of this solution contains 0,01 mg of selenium.

4.6 Pure iron, containing less than 0,000 1 % (mass fraction) of selenium

5 Apparatus

All volumetric glassware shall be Class A and calibrated, in accordance with ISO 648 or ISO 1042 as appropriate.

Before use, all glassware shall be cleaned by boiling with hydrochloric acid to remove any chemical contamination.

5.1 Auto sampler equipped with micropipettes of capacity 10 μl to 50 μl

5.2 Atomic absorption spectrometer and electrothermal atomizer

This shall be equipped with a selenium hollow-cathode lamp or an electrodeless discharge lamp and supplied with pure argon.

The instrument shall be fitted with Zeeman effect background correction.

An electrothermal atomizer equipped with a L'vov platform, mounted in a pyrolytically coated graphite tube, supplied with argon as purge gas, is recommended.

The characteristic mass for selenium shall be less than 30 pg of selenium.

6 Sampling

Sampling shall be carried out in accordance with EN ISO 14284 or with an appropriate national standard for steels.

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7 Procedure

7.1 Test portion

According to the expected selenium content (x) of the test sample, weigh to the nearest 0,1 mg, a test portion as indicated in Table 1.

Table 1 — Mass of the test portion

Expected selenium content (x) of the test sample (µg/g)	Mass of the test portion (mg)
x < 15	2 000
15 ≤ x < 35	1 000
35 ≤ x < 75	400
75 ≤ x < 150	200
150 ≤ x ≤ 200	100

7.2 Blank test

Carry out a blank test simultaneously with the determination, following the same procedure and using the same quantities of all reagents as used for the determination, but substituting pure iron (4.6) for the test portion.

7.3 Preparation of the test solution

Transfer the test portion (7.1) into a 250 ml beaker tall form. Cover the beaker with a watch glass and add 10 ml of water, 10 ml of nitric acid (4.1) and 30 ml of hydrochloric acid (4.2).

Heat at a temperature just below the boiling point (approximately 150 °C) during at least two hours. Allow to cool. If necessary, filter through a medium texture filter paper and collect the filtrate in a 250 ml one-mark volumetric flask. Wash the filter paper several times with hot water and collect the washings in the same 250 ml volumetric flask.

Allow to cool, dilute to the mark with water and mix.

7.4 Preparation of the standard addition solutions for the test solution

Into a series of 50 ml one-mark volumetric flasks introduce 25 ml aliquots of the test solution (7.3) and add the volumes of selenium standard solution (4.5) shown in Table 2. Dilute to the mark with water and mix.

These solutions are labelled S1, S2, S3 and S4 respectively.

Table 2 — Standard addition solutions for the test solution

Label of the solution	Selenium standard solution volume µl	Concentration of selenium in the test addition solutions µg/ml
S1	0	0
S2	200	0,04
S3	400	0,08
S4	600	0,12

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7.5 Preparation of the standard addition solutions for the blank test

Into a series of 50 ml one-mark volumetric flasks introduce 25 ml aliquots of the blank solution (7.2) and add the volumes of selenium standard solution (4.5) shown in Table 3. Dilute to the mark with water and mix.

These solutions are labelled B1, B2, B3 and B4 respectively.

Table 3 — Standard addition solutions for the blank test

Label of the solution	Selenium standard solution volume µl	Concentration of selenium in the test addition solutions µg/ml
B1	0	0
B2	200	0,04
B3	400	0,08
B4	600	0,12

8 Measurements

Set the required instrument parameters and align the electrothermal atomiser according to the manufacturer's instructions (see NOTE 1 and 2).

Adjust the wavelength in the region of 196,0 nm to minimum absorbance.

NOTE 1   The operating parameters for electrothermal atomic absorption spectrometry vary considerably from an instrument to another and much more than for flame atomic absorption spectrometry. Typical operating parameters are given in Annex A. Annex B details the instruments and the instrumental conditions used by the laboratories having participated to the interlaboratory test programme (see Clause10).

Fill the auto sampler with the blank standard addition solutions (7.5), the test standard addition solutions (7.4) and the matrix-modifier (4.3.1 or 4.3.2).

Inject sequentially 10 µl of each of the solutions 7.5 and 7.4 and add to each solution 10 µl of the matrix modifier (4.3.1 or 4.3.2). Measure the absorbance of each solution at the adjusted wavelength. Correct the absorbances for background simultaneously.

NOTE 2   In general the absorbance is measured by peak height or peak area. The determination by peak area is recommended.

9 Expression of results

9.1 Plotting of the standard addition graphs

Plot the absorbances corresponding to the blank standard addition solutions against the concentration of selenium added, expressed in µg/ml.

Plot the absorbances corresponding to the test standard addition solutions against the concentration of selenium added, expressed in µg/ml.

Use least squares regression method to calculate the lines for the blank standard addition solutions and for the test standard addition solutions.

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9.2 Method of calculation

Determine the concentrations of selenium, expressed in µg/ml, in the test solution and in the blank test C_S and C_B as the two intercepts on the concentration axis (see 9.1).

The difference (C_S - C_B) gives the net concentration of selenium in the test solution (solution S1).

Calculate the selenium mass fraction, in per cent (%), as follows:

$$W_{Se} = \frac{(C_S - C_B) \times 2 \times 250 \times 100}{m \times 1000}$$

where:

W_{Se}	is the selenium mass fraction in per cent (%);
C_S	is the selenium concentration in the test solution, in micrograms per millilitre (µg/ml);
C_B	is the selenium concentration in the blank test solution, in micrograms per millilitre (µg/ml);
m	is the mass of the test portion, in milligrams (mg).

10 Precision

Four laboratories in four European countries participated in an inter laboratory test programme under the auspices of ECISS/TC 102/WG 3, involving three determinations of selenium at nine levels.

Each laboratory carried out two determinations under repeatability conditions as defined in ISO 5725-1, i.e. one operator, same apparatus, identical operating conditions, same standard addition solutions and a minimum period of time. The third determination was carried out on a different day using the same apparatus with different standard addition solutions.

Details on the samples used are given in Annex C and the results obtained are reported in Annex D.

The sets of data available were too few for a statistical evaluation based on ISO 5725-2 and ISO 5725-3 and CEN/TR 10345. Only Mandel's h and k statistics were used (see Figures D.1 and D.2) rather for illustrative purposes.

Annex D also provides some considerations on the data presented.

11 Test report

The test report shall contain the following information:

a) identification of the test sample;

b) method used;

c) results;

d) any unusual characteristics noted during the determination;

e) any operation not included in this Technical Report or in the document to which reference is made or regarded as optional;

f) date of the test and/or date of preparation or signature of the test report;

g) signature of the responsible person.

Annex A
(informative)

Typical operating parameters

A.1 Typical conditions for the determination of selenium by electrothermal atomic absorption spectrometry

Injection volumes 10 μl of the test standard addition solutions and of the blank standard addition solutions and 10 μl of the matrix modifier solution;

Matrix modifier Pd-Ni or Pd-Mg;

Instrumental settings See Table A.1

Table A.1 — Instrumental settings

Wavelength nm	Slit width nm	Ashing temperature °C	Atomisation temperature °C
196,0	0,7	500	2000

Background Correction: Zeeman effect;

Typical temperature profile: see Table A.2;

Table A.2 — Typical temperature profile

Step	Temperature °C	Ramp s	Hold s	Gas flow ml/min	Read
1	100	10	10	300	
2	140	10	20	300	
3	500	10	20	300	
4	2000	0	4	0	YES
5	2800	10	2	300	

Measurement mode: Peak area;

Integration time: 4 s.

A.2 Performance criteria

Detection limit 0,02 μg/ml Se

Characteristic mass < 30 pg Se

Maximum concentration 0,4 μg/ml Se

A.3 Criterion for graph linearity

A.3.1 General

In the case of standard addition method, the graph linearity should be checked as described in A.3.2 and A.3.3.