SLOVENSKI STANDARD
SIST EN 14945:2006

01-maj-2006

Ognjevzdrģni izdelki in materiali ï Spektrometrijsko doloļ evanje kroma (VI) v kromovih ognjevzdrģnih nosilcih, pred uporabo in po njej

Refractory products and materials - Spectrometric determination of chromium (VI) in chrome bearing refractories, before and after use

Feuerfeste Erzeugnisse und Werkstoffe - Spektrometrische Bestimmung des Chrom(VI)-Gehaltes in chromhaltigen feuerfesten Erzeugnissen vor und nach der Verwendung

Produits et matériaux réfractaires - Détermination par spectrométrie du chrome VI dans des matériaux réfractaires a forte teneur en chrome, avant et apres usage

Ta slovenski standard je istoveten z: **EN 14945:2005**

ICS:

81.080	Ognjevzdržni materiali	Refractories

SIST EN 14945:2006 **en**

EUROPEAN STANDARD

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English Version

Refractory products and materials - Spectrometric determination of chromium (VI) in chrome bearing refractories, before and after use

Produits et matériaux réfractaires - Détermination par spectrométrie du chrome VI dans des matériaux réfractaires à forte teneur en chrome, avant et après usage	Feuerfeste Erzeugnisse und Werkstoffe - Spektrometrische Bestimmung des Chrom(VI)-Gehaltes in chromhaltigen feuerfesten Erzeugnissen vor und nach der Verwendung

This European Standard was approved by CEN on 19 September 2005.

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 Central Secretariat 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 Central Secretariat has the same status as the official versions.

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

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Contents

Foreword

This European Standard (EN 14945:2005) has been prepared by Technical Committee CEN/TC 187 “Refractory products and materials”, the secretariat of which is held by BSI.

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 2006, and conflicting national standards shall be withdrawn at the latest by June 2006.

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

1 Scope

This European Standard describes a method for the spectrometric determination of chromium (VI) in chrome bearing refractories, before and after use. It is applicable to fired magnesia-chrome products (containing natural chromite, fused grain or co-clinker) and to unfired materials (with refractory cement or chemical bonds) although it is not to be restricted to these types of refractory. The method is applicable to concentrations up to 500 mg/kg of chromium (VI).

This range may be extended or reduced by modifying the dilution factors.

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.

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696:1987)*

3 Principle

Hexavalent chromium is extracted from the sample using a solution of 2 % (w/v) NaOH / 3 % (w/v) Na_2CO_3 which dissolves the common hexavalent chromium compounds potentially present (Ca, Fe, Na, K, Mg, Zn, Cu, Pb) but not their trivalent counterparts.

The chromium (VI) is then determined spectrometrically by reaction with 1,5 - diphenyl carbazide which forms a red-violet chromium complex. The absorbance of the complex is measured at a wavelength between 540 nm and 550 nm, the exact wavelength being given in the test report.

NOTE It is recognized that the method does not entail total dissolution of the test sample and hence not all the chromium (VI) may be taken into solution. Trials have indicated that the method yields a minimum of 80 % of the total chromium (VI) present and an inter-laboratory reproducibility of ± 15 % of content. Should a more accurate assessment of chromium (VI) be required, repeat leachings can be carried out.

4 Apparatus

4.1 Analytical balance, capable of being read to ± 0,000 5 g.

4.2 Laboratory volumetric glassware, grade A.

4.3 Spectrophotometer, suitable for use in the 540 nm to 550 nm wavelength range.

4.4 Jaw crusher, for crushing bulk samples.

4.5 Device for fine grinding.

4.6 Magnet.

4.7 Hot plate magnetic stirrer.

5 Reagents

5.1 General

Use only reagents of recognized analytical grade and only distilled or deionized water with an electrical conductivity less than 2 µS/cm, or conforming to the requirements of Grade 3 of EN ISO 3696.

NOTE Commercially available reagents with guaranteed concentrations may also be used.

5.2 Alkaline extraction solution

Dissolve 30 g sodium carbonate (Na_2CO_3) and 20 g sodium hydroxide pellets (NaOH) in water and dilute to volume in a 1 l volumetric flask. Mix thoroughly. Prepare this solution on the day of use.

5.3 Chromium (VI) stock solution

Weigh (0,355 ± 0,005) g of potassium dichromate ($K_2Cr_2O_7$) dried at (110 ± 10) °C and dissolve in approximately 200 ml of water in a 500 ml volumetric flask. Dilute to volume.

This solution is stable indefinitely and contains (250 ± 4) mg/l of chromium.

5.4 Chromium (VI) standard solution

Using a pipette transfer 10 ml of the chromium (VI) stock solution (see 5.3) to a 500 ml volumetric flask and dilute to volume with water. This solution contains 5 mg/l of chromium. Prepare this solution on the day of use.

CAUTION — Do not pipette by mouth.

5.5 1,5-Diphenyl carbazide solution

Dissolve 1 g of 1,5-diphenyl carbazide in 100 ml of propanone (acetone) C_3H_6O. Acidify with one drop of glacial acetic acid. Prepare this solution on the day of use.

5.6 1+1 Sulphuric acid (*V*/*V*)

6 Sampling

Using a Jaw crusher (4.4), reduce the bulk sample to a size suitable for fine grinding. Cone and quarter approximately 200 g of the crushed sample. Remove any iron introduced from the jaw crusher using a magnet. Fine grind the sample to reduce its particle size so that approximately 90 % is less than 125 µm.

NOTE 1 Dust masks and skin protection should be worn and, if possible, localized dust extraction used during sample preparation.

NOTE 2 Iron contamination from jaw crushing could potentially cause reduction of chromium (VI) during the analysis if not removed.

NOTE 3 The removal of any metal or slag adhering to the sample by using a chisel or dry cutting is advisable, as their presence may result in the reduction of chromium (VI) during analysis.

NOTE 4 Iron or steel mortars should not be used for fine grinding to avoid contamination of the sample by metallic iron.

7 Calibration

To a series of 7 100 ml volumetric flasks add 0 ml, 2 ml, 5 ml, 10 ml, 15 ml, 20 ml, and 25 ml of chromium (VI) standard solution (5.4).

Add sufficient water to each flask to bring the volume to approximately 50 ml. Acidify each with 5 drops of sulphuric acid (5.6). Allow to cool.

Add 10 ml of 1,5-diphenyl carbazide solution (5.5) and dilute to 100 ml.

Mix well and allow to stand for 5 min for the colour to develop fully, and measure within a further 10 min.

Measure the absorbance between 540 nm and 550 nm against water in 10 mm glass cells.

Plot the absorbance against chromium (VI) concentration of the above solutions. The resulting graph will give a concentration range of 0 mg/kg to 500 mg/kg chromium (VI) when using the procedure described in Clause 8.

8 Procedure

Weigh (5 ± 0,1) g of the fine ground sample to the nearest ± 0,005 g after drying at (110 ± 10) °C. Transfer into a 600 ml beaker and add 200 ml of the boiling alkaline extraction solution (5.2). Cover the beaker with a watch glass and boil with constant stirring for 30 min using a hot plate magnetic stirrer (to keep the sample in suspension). Do not allow it to evaporate to dryness.

Allow to cool to ambient temperature. Filter the extract through a coarse filter paper[1], pre-washed with cold extraction solution (5.2), into a 500 ml volumetric flask. Wash the residue twice with 50 ml aliquots of the extraction solution followed by water to a total volume of about 400 ml. Dilute to 500 ml with water.

Pipette a 25 ml aliquot portion into a 250 ml beaker. Acidify by the dropwise addition of sulphuric acid (5.6), stirring until the evolution of carbon dioxide ceases, then add a further 5 drops of sulphuric acid. Allow to cool to ambient temperature, then transfer to a 100 ml volumetric flask, add 10 ml of 1,5-diphenyl carbazide solution (5.5) and dilute to 100 ml.

Allow the colour to develop for 5 min and measure the absorbance within a further 10 min at the wavelength used for the calibration (see Clause 7) using water in the reference cell and 10 mm glass cells. Do not allow to stand longer than 15 min after the addition of the 1,5 diphenyl carbazide as the colour of the solution can be affected.

If the filtrate is discoloured or turbid, take another aliquot portion omitting the 1,5-diphenyl carbazide solution and measure its absorbance as a correction.

Estimate the concentration of chromium (VI) from the calibration graph described in Clause 7.

NOTE 1 With high alumina materials, cloudiness may occur on acidification or after addition of 1,5-diphenyl carbazide solution. In the first case, the cloudiness may disappear after agitation and in the second, may be removed by the addition of a few further drops of sulphuric acid.

NOTE 2 The range can be extended up to 1 250 mg/kg by using a 10 ml aliquot of extraction filtrate.

NOTE 3 The presence of organic species in the test sample may interfere with the method.

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[1] A Whatman No.40 filter paper has been found suitable.