SLOVENSKI STANDARD
kSIST-TP FprCEN/TR 16895:2015

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Jeklene in železove litine - Ugotavljanje svinca, kadmija, živega srebra, šestvalentnega kroma, polibromiranih bifenilov (PBB) in polibromiranih difeniletrov (PBDE) v zvezi z direktivami 2011/65/EU (RoHS) in 2000/53/ES (ELV) - Omejitve

Steels and cast irons - Determination of lead, cadmium, mercury, hexavalent chromium, polybrominated biphenyls (PBB) and polybrominated diphenylethers (PBDE) with regard to directives 2011/65/EU (RoHS) and 2000/53/EC (ELV) - Limitations

Aciers et fontes - Déterminations du plomb, du cadmium, du mercure, du chrome hexavalent, des diphényles polybromés (PBB) et des diphenyléthers polybromés (PBDE) en relation avec les directives 2011/65/EU (RoHS) et 2000/53/EC (ELV) - Limites

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77.040.30	Kemijska analiza kovin	Chemical analysis of metals
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Steels and cast irons - Determination of lead, cadmium, mercury, hexavalent chromium, polybrominated biphenyls (PBB) and polybrominated diphenylethers (PBDE) with regard to directives 2011/65/EU (RoHS) and 2000/53/EC (ELV) - Limitations

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
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Foreword

This document (FprCEN/TR 16895:2015) 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.

This document is currently submitted to the Technical Committee Approval.

1 Scope

The present Technical Report gives guidance regarding the chemical composition controls of steels (except chrome plated products) and cast irons in respect of the European legislation, namely Directives 2011/65/EU (RoHS) [1], repealing 2002/95/EU and 2000/53/EC (ELV) [2].

These directives require the characterization of these materials for Cd, Cr (VI), Hg, Pb, polybrominated biphenyls (PBB) and polybrominated diphenylethers (PBDE). Nevertheless, the directives do not reflect the correspondence between these elements/compounds and the normal composition of each material concerned. In other words, for every material there is an obligation to determine all the compounds listed, independently of the relevance of such controls.

2 Requirements and applicability

2.1 General

Directive 2011/65/EU, article 4, restricts the following substances to the maximum concentration values:

— Lead: 0,1 %;

— Mercury: 0,1 %;

— Cadmium: 0,01 %;

— Hexavalent chromium: 0,1 %;

— Polybrominated biphenyls (PBB): 0,1 %;

— Polybrominated diphenyl ethers (PBDE): 0,1 %.

Steel and cast iron manufacturers are often required to state/provide compliance with the directives above and submit analytical results for each of those compounds. However, due to the manufacturing processes and the inherent properties of the materials of concern, the determination of most of the compounds listed is not applicable or relevant.

Subclauses 2.2 and 2.3 detail on the relevance of these requirements.

2.2 Bulk materials

2.2.1 Lead (Pb)

Due to a 1 755 °C boiling point, lead is the single element among the six compounds specified in the directives which can be present in the materials.

NOTE For stainless steel production using the Argon Oxygen Decarburization (AOD) converter process or equivalent, the lead content in the alloy will be considerably decreased to orders of magnitude below the directive's requirement's levels.

In contrast to cadmium and mercury, lead is also possible to detect and quantify on a reproducible base by using standardized methods as EN 10181 [3], EN 62321 [4], EN 62321-1 [5] and ISO 16918-1 [6].

2.2.2 Cadmium (Cd) and Mercury (Hg)

Due to the high temperature required during the melting processes and because of their physic-chemical properties, cadmium (Cd) and mercury (Hg) are normally absent in steels and cast irons.

The temperature required for melting iron based alloys is at least 1 400 °C, whereas the boiling temperatures of Cd and Hg are 767 °C and 357 °C respectively. In other words, these elements will evaporate during the melting process and cannot be present in an easily quantifiable amount in the materials.

There are analytical techniques available and appropriate for the determination of both these elements below 1 µg/g as for example inductively coupled plasma mass spectrometry (ICP-MS), cold vapour atomic absorption spectrometry or electrothermal atomic absorption spectrometry (ETAAS). However for the physical reasons above, i.e. the “absence of content”, it remains impossible to verify the robustness of the procedures for such aims: this includes selecting the most appropriate dissolution procedures and also the unavailability of appropriate reference materials.

2.2.3 Hexavalent chromium [Cr (VI)]

According to the Document “Hexavalent Chromium in steels, cobalt-, nickel and zirconium based alloys” [7] the occurrence of Cr(VI) in steel is purely hypothetical. This is due to the physical nature of metallic bonding where ions cannot exist.

2.2.4 Polybrominated biphenyls (PBB) and polybrominated diphenylethers (PBDE)

The most common types of PBB and PBDE homologues are penta-, octo- and deca- bromodiphenyl ethers and hexa-, octo- and deca- bromobiphenylethers. They are extremely stable compounds with boiling points in the range of about 300 to 500 °C. Investigations [8] have shown that PBBs decompose by pyrohydrolysis at temperatures ranging from 600 to 900 °C, i.e. significantly lower than in the steel making process and that the main part of PBDEs in fly ash from electric arc furnaces are destroyed or removed by thermal treatment at 1 450 °C [9].

Thus it shall be concluded that these compounds cannot be present in the steel (or cast iron) itself.

2.3 Surface

2.3.1 General

The as-delivered products from the steel plants or foundries are controlled and protected.

However, as for any material, the surface of steel and cast iron products may get contaminated or may undergo surface reactions. In some circumstances, due to further processing or treatments, this may result in presence of un-wanted substances on the surface.

2.3.2 Hexavalent chromium [Cr(VI)]

Due to some surface treatment hexavalent chromium is the single substance among the six compounds specified in the directives which may be found on the surface of the material.

However a positive detection of this ion on the surface of a material shall not be put in correspondence with the bulk material composition. For the control of this ion, standardized methods are available as, for example, EN 62321.

3 Recommendation

When receiving requirements related with Directives 2011/65/EU (RoHS), 2002/95/EU and 2000/53/EC, it is recommended to take the information given in the present Technical Report into account.

In other words the single compounds relevant to be determined are:

— lead in the bulk materials (see NOTE in 2.2.1);

— hexavalent chromium on the surface of some products (see 2.3.2).

Bibliography

[1] Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS)

[2] Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles (ELV)

[3] EN 10181, *Chemical analysis of ferrous materials — Determination of lead in steels — Flame atomic absorption spectrometric method*

[4] EN 62321, *Electrotechnical products — Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers) (IEC 62321)*

[5] EN 62321-1, *Determination of certain substances in electrotechnical products — Part 1: Introduction and overview (IEC 62321-1)*

[6] ISO 16918-1, *Steel and iron — Determination of nine elements by the inductively coupled plasma mass spectrometric method — Part 1: Determination of tin, antimony, cerium, lead and bismuth*

[7] Hexavalent Chromium in steels, cobalt, nickel and zirconium based alloys, issued by Swerea KIMAB

[8] IPCS/INCHEM, International Programme on Chemical Safety, Health and Safety Guide No. 83

[9] Yi.Ming Lin, Shao-Qi Zhou et.al. Emissions of polybrominated diphenyl ethers during the thermal treatment for electric arc furnace fly ash, Aerosol and Air quality Research, 12: 237-250, 2012