SLOVENSKI STANDARD
SIST EN 16136:2015

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Nadomešča:
SIST EN 16136:2012

Goriva za motorna vozila - Določevanje mangana in železa v neosvinčenem motornem bencinu - Metoda z optično emisijsko spektrometrijo z induktivno sklopljeno plazmo (ICP OES)

Automotive fuels - Determination of manganese and iron content in unleaded petrol - Inductively coupled plasma optical emission spectrometry (ICP OES) method

Kraftstoffe für Kraftfahrzeuge - Bestimmung des Mangan- und Eisengehaltes in unverbleitem Ottokraftstoff - Optische Emissionsspektrometrie mit induktiv gekoppeltem Plasma (ICP OES)

Carburants pour automobiles - Détermination des teneurs en fer et en manganèse dans les essences sans plomb - Méthode spectrométrique optique par plasma à couplage inductif (ICP OES)

Ta slovenski standard je istoveten z: **EN 16136:2015**

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71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis
75.160.20	Tekoča goriva	Liquid fuels

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EUROPEAN STANDARD

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Supersedes EN 16136:2011

English Version

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This European Standard was approved by CEN on 12 December 2014.

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

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Foreword

This document (EN 16136:2015) has been prepared by Technical Committee CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin”, the secretariat of which is held by NEN.

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of an identical text or by endorsement, at the latest by August 2015, and conflicting national standards shall be withdrawn at the latest by August 2015.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 16136:2011.

The major updates are the lowering of the manganese content to allow a specification setting of 2 mg/l of manganese in line with the FQD requirement per 2014-01-01, and the introduction in the scope of determination of iron content, which can be added into petrol as ferrocene.

This document answers requirements originating from the amended Fuels Quality Directive (FQD, [2]).

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

1 Scope

This European Standard specifies a method based on inductively coupled plasma optical emission spectrometry (ICP OES) for the determination of manganese content from about 0,5 mg/l to about 7,5 mg/l and of iron content from about 1,4 mg/l to about 6,0 mg/l in unleaded petrol containing up to 3,7 % (*m*/*m*) oxygen.

WARNING — The use of this European Standard may involve hazardous materials, operations and equipment. This European Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this European Standard to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

NOTE 1 Manganese as MMT and iron as ferrocene are added to petrol to increase anti-knock properties.

NOTE 2 Solutions of MMT in petrol are unstable when exposed to light. Low and erratic results are expected if petrol samples are exposed to light prior the analysis.

Iron and manganese contents higher than 6,0 mg/l and 7,5 mg/l respectively may be measured after preliminary dilution of the sample with a suitable solvent. However, the precision has not been established for such a procedure. Further work regarding automotive ethanol (E85) fuel is on-going in CEN.

NOTE 3 For the purposes of this European Standard, the terms "% (*m*/*m*)" and "% (*V*/*V*)" are used to represent the mass fraction (μ) and the volume fraction (φ) of a material respectively.

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

EN ISO 3170, *Petroleum liquids — Manual sampling (ISO 3170)*

EN ISO 3171, *Petroleum liquids — Automatic pipeline sampling (ISO 3171)*

EN ISO 3675, *Crude petroleum and liquid petroleum products — Laboratory determination of density — Hydrometer method (ISO 3675)*

EN ISO 12185, *Crude petroleum and petroleum products — Determination of density — Oscillating U-tube method (ISO 12185)*

3 Principle

A petrol sample is diluted with a hydrocarbon solvent. The solution is introduced directly into the plasma of an ICP OES spectrometer. Iron and manganese contents are calculated by comparison with calibration solutions prepared from suitable iron and manganese compounds. An internal standard is employed to correct viscosity and vapour pressure effects.

4 Reagents

Unless specified otherwise, only chemicals which are known to have a high degree of purity shall be used.

Some ready-made commercial multi-element Standard solutions may be used instead of the single element Standard solution (4.4 and 4.5).

IMPORTANT — In the case of using several mono-element Standard solutions, attention shall be paid to ensure that they are free of other analyte elements.

4.1 Kerosene, boiling range between 150 °C and 250 °C, analytical reagent grade.

Other grades of kerosene with analyte concentrations below the detection limit of the instrument for the elements under investigation may be used. In this case, perform a wavelength scan for analyte elements to check spectral interferences.

4.2 Heptane, analytical reagent grade.

4.3 Solvent, add 25 ml heptane (4.2) to a 500 ml HDPE bottle (5.1.2) and fill to 500 ml with kerosene (4.1).

4.4 Manganese Standard solution, commercially available in oil, c(Mn) = 100 mg/kg.

4.5 Iron Standard solution, commercially available in oil, c(Fe) = 100 mg/kg.

Some commercial element Standard solutions are furnished with higher content on the market. Those solutions may be used instead of the required solutions, but an initial mass to mass dilution has to be done according to recommendations given in 7.4.

4.6 Element Standard solution, of one of the elements cobalt, scandium, yttrium, etc. commercially available in oil (analyte free), for example with 1 000 mg/kg per element, available as single element standards.

NOTE The internal Standard solutions are commonly available as single element standards with various element contents.

4.7 Argon, with a purity of ≥ 99,995 % (*V/V*).

Small amounts of oxygen (purity ≥ 99,995 % (*V/V*)) may be added, for instance in accordance with the operating instructions of the equipment manufacturer, to the argon gas stream using a metering valve (30 ml/min to 100 ml/min) to prevent carbon deposits in the area of the plasma torch.

5 Apparatus

5.1 Laboratory equipment:

All glassware shall be cleaned carefully before use.

5.1.1 Glassware, usual laboratory glassware, together with the following:

5.1.1.1 Beakers, 50 ml.

5.1.1.2 Volumetric flasks, 20 ml, 50 ml and 500 ml according to EN ISO 1042, with taper sleeve and plug.

5.1.2 Bottles, 50 ml and 500 ml, with screw caps, high-density polyethylene (HDPE).

5.1.3 Graduated pipettes or variable volume automatic pipettes, fitted with disposable polypropylene tips capable to measure up to the nearest 0,01 ml.

CAUTION — Attention shall be paid with air displacement pipettes in the presence of volatile solvents or petrol samples.

5.2 Analytical balance, capable of weighing to the nearest 0,1 mg.

5.3 ICP OES spectrometer:

ICP OES spectrometer equipped for the analysis of organic liquids, with a high-frequency generator and a nebulizer suitable for organic solvents. The use of a feed pump for sample introduction into the nebulizer is required. Both setup and operation of the ICP OES spectrometer shall be done in accordance with operating instructions of the manufacturer.

A cooled spray chamber may be used, provided that the temperature is controlled ± 1 °C.

Table 1 gives the recommended wavelengths. As the magnitude of the background signal highly depends on spectral structures caused by the sample's nature, only net intensities are to be recorded.

Table 1 — Recommended wavelengths

Element	Wavelength nm
Manganese	257,610 259,372 260,569 279,482 279,827 293,931
Iron	234,350 238,204 240,488 259,940 261,187
Cobalt	238,892
Scandium	361,383
Yttrium	224,306 360,073 371,029

6 Sampling

IMPORTANT — The laboratory shall receive a sample which is truly representative and was not damaged or altered during transport or storage.

Unless otherwise specified in the commodity specification, samples shall be taken as described in EN ISO 3170 or EN ISO 3171 and/or in accordance with the requirements of national regulations for the sampling of the product under test.

The samples shall be stored in clean, opaque containers.

7 Preparation of solutions

7.1 General

In order to avoid inhomogeneity, iron and manganese standard solutions (4.4 and 4.5) shall be shaken vigorously before use. It is strongly advised to use freshly prepared calibration solutions.

7.2 Preparation of the internal standard solution

Weigh 2,00 g of cobalt, scandium or yttrium stock solution (4.6) with a precision of 0,01 g in a 50 ml volumetric flask (5.1.1.2)

Fill up to 50 ml with kerosene (4.1).

This prepared solution shall be homogenized by vigorous shaking.

The same standard batch shall be used for all samples and calibration standards.

7.3 Preparation of the manganese intermediate solution

Weigh 1,50 g ± 0,01 g of manganese standard solution (4.4) into a 50 ml HDPE bottle (5.1.2). Add solvent (4.3) to 15,00 g ± 0,01 g. In case manganese standard solutions (4.4) with different manganese content are used, the mass of standard solution shall be adjusted accordingly to achieve 10 mg/kg manganese content.

7.4 Preparation of the iron intermediate solution

Weigh 1,50 g ± 0,01 g of iron standard solution (4.5) into a 50 ml HDPE bottle (5.1.2). Add solvent (4.3) to 15,00 g ± 0,01 g. In case iron standard solutions (4.5) with different iron content are used, the mass of standard solution shall be adjusted accordingly to achieve 10 mg/kg iron content.

7.5 Preparation of the calibration solutions

The calibration solutions shall be prepared as indicated in Table 2. Each mass of manganese intermediate dilution solution (7.3) and iron intermediate dilution solution (7.4), shall be weighed to the nearest 0,001 g into a 20 ml volumetric flask (5.1.1.2). Add exactly 1,00 ml of the internal standard solution (7.2). Fill with solvent (4.3) to the mark.

NOTE These concentrations in Table 2 seem odd compared to the scope of determination as given in Clause 1, but in 9.1 a dilution step for the sample is introduced.

All solutions thus prepared shall be homogenized by vigorous shaking.

The exact concentration of the calibration solution shall be calculated considering the exact weighed portion.

Table 2 — Concentration of manganese and iron in the calibration solutions

Calibration solutions	Manganese intermediate solution (7.3) g	Iron intermediate solution (7.4) g	Manganese concentration mg/l	Iron concentration mg/l
Blank	0,00	0,00	0,00	0,00
1	0,05	0,05	0,025	0,025
2	0,20	0,20	0,10	0,10
3	0,50	0,50	0,25	0,25
4	0,80	0,80	0,40	0,40

7.6 Preparation of quality control solution

A 0,15 mg/l quality control (QC) solution shall be prepared to verify sensitivity and accuracy of the calibration curve.