SLOVENSKI STANDARD
SIST EN 16135:2012

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Goriva za motorna vozila - Določevanje mangana v neosvinčenem motornem bencinu - Metoda plamenske atomske absorpcijske spektrometrije (AAS)

Automotive fuels - Determination of manganese content in unleaded petrol - Flame atomic absorption spectrometric method (AAS)

Kraftstoffe für Kraftfahrzeuge - Bestimmung des Mangangehalts in unverbleitem Ottokraftstoff - Atomabsorptionsspektrometrisches Verfahren (AAS)

Carburants pour automobiles - Détermination de la teneur en mangane dans les essences sans plomb - Méthodes par spectrométrie d'absorption atomique (SAA)

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75.160.20	Tekoča goriva	Liquid fuels

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English Version

Automotive fuels - Determination of manganese content in unleaded petrol - Flame atomic absorption spectrometric method (FAAS)

Carburants pour automobiles - Détermination de la teneur en manganèse dans les essences sans plomb - Méthode par spectrométrie d'absorption atomique de flamme (FAAS)

Kraftstoffe für Kraftfahrzeuge - Bestimmung des Mangangehalts in unverbleitem Ottokraftstoff - Flammenatomabsorptionsspektrometrisches Verfahren (FAAS)

This European Standard was approved by CEN on 29 October 2011.

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Foreword

This document (EN 16135:2011) 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of an identical text or by endorsement, at the latest by June 2012, and conflicting national standards shall be withdrawn at the latest by June 2012.

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 answers requirements originating from the amended Fuels Quality Directive [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, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies a method based on flame atomic absorption spectrometry (FAAS) for the determination of manganese content present as methylcyclopentadienyl manganese tricarbonyl (MMT [1)]) in unleaded petrol from about 2 mg/l to about 8 mg/l. This test method is applicable to unleaded petrol containing up to 3,7 % (*m*/*m*) oxygen, including those with ethanol up to 10 % (*V*/*V*).

NOTE 1 Manganese as MMT is added to petrol to increase antiknock properties.

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

NOTE 3 Manganese contents higher than 8 mg/l can be measured after preliminary dilution of the sample with a suitable solvent. However, the precision has not been established for such procedure.

NOTE 4 Application to the determination of other manganese compounds in unleaded petrol has not been tested.

NOTE 5 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 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 648, *Laboratory glassware — Single-volume pipettes (ISO 648:2008)*

EN ISO 1042, *Laboratory glassware — One-mark volumetric flasks (ISO 1042:1998)*

EN ISO 3170, *Petroleum liquids — Manual sampling (ISO 3170:2004)*

EN ISO 3171, *Petroleum liquids — Automatic pipeline sampling (ISO 3171:1988)*

EN ISO 3675, *Crude petroleum and liquid petroleum products — Laboratory determination of density — Hydrometer method (ISO 3675:1998)*

EN ISO 12185, *Crude petroleum and petroleum products — Determination of density — Oscillating U-tube method (ISO 12185:1996)*

3 Principle

A portion of petrol sample is diluted with a hydrocarbon solvent. The solution is then aspirated into the air/acetylene flame of an atomic absorption spectrometer. The absorbance is measured at 279,5 nm. Manganese content is calculated by comparison with calibration solutions prepared from suitable manganese compounds.

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1) MMT is a registered trademark of Ethyl Corporation.

4 Reagents

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

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

NOTE Other grades of kerosene with analyte concentration below the detection limit of the instrument and screened by performing a wavelength scan for analyte elements may be used.

4.2 2,2,4-trimethylpentane (iso-octane), analytical reagent grade.

4.3 Xylene (mixture of isomers), analytical reagent grade.

4.4 Solvent, add 25 ml *iso*-octane (4.2) and 25 ml xylene (4.3) to a 50 ml glass bottle (5.1.3) and mix thoroughly.

4.5 Manganese standard solution, dissolved in oil, *c*(Mn) = 1 000 mg/kg.

NOTE 1 A multi-element standard solution may also be used instead of the single element standard solution.

NOTE 2 Some element standard solutions are supplied with different element content on the market. These solutions may be used instead of the required solutions, but an initial mass to mass dilution has to be done.

4.6 Manganese intermediate solution, *c*(Mn) = 20 mg/kg. Weigh 0,50 g ± 0,01 g of manganese standard solution (4.5) into a 50 ml bottle (5.1.3). Add kerosene (4.1) to 25,00 g ± 0,01 g. Each mass shall be weighed to the nearest 0,1 mg.

In case manganese standard solutions (4.5) with different manganese content are used, the mass of standard solution shall be adjusted accordingly to achieve 20 mg/kg manganese content.

4.7 Air, oil free, under pressure in a steel cylinder, or compressed air.

4.8 Acetylene, 99,0 % min., under pressure in a steel cylinder.

5 Apparatus

5.1 Laboratory equipment

5.1.1 General

All glassware shall be cleaned carefully before use.

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

5.1.2.1 Beakers, 50 ml.

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

5.1.3 Bottles, 50 ml, with screw caps, high-density polyethylene (HDPE).

5.1.4 Two-mark pipette, capacity 5 ml, conforming to class A of EN ISO 648, with suction ball, or alternatively **graduated pipettes or variable volume automatic pipettes,** fitted with disposable polypropylene tips.

CAUTION — Attention shall be paid during the use of 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 Flame atomic absorption spectrometer, equipped with manganese hollow cathode lamp or lamp emitting specific radiation of manganese, fitted with a burner head for acetylene and air flame, and suitable for use with organic solutions.

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 filled into clean containers.

7 Preparation of solutions

7.1 General

In order to avoid inhomogeneity, all calibration solutions shall be shaken vigorously before use. It is strongly advised to use freshly prepared calibration solutions.

7.2 Preparation of the calibration and quality control solution

The calibration solutions and the Quality Control (QC) solution shall be prepared as indicated in Table 1. The mass of the manganese intermediate solution (4.6) shall be weighed to the nearest 0,1 mg in a 20 ml volumetric flask (5.1.2.2). For each calibration solution, add 5,0 ml of the solvent (4.4) and fill with kerosene (4.1) to the mark. Calibration solutions shall be homogenized by shaking.

Table 1 — Concentration of manganese in calibration and quality control solutions

Calibration solutions	Manganese intermediate solution g	Manganese concentration mg/l
blank	0,0	0,00
1	0,2	0,2
2	0,5	0,5
3	1,0	1,0
4	1,5	1,5
5	2,0	2,0
QC	1,0	1,0

8 Calibration

8.1 Preparation of instrument

8.1.1 Switch on the atomic absorption spectrometer (5.3) following the manufacturer instruction. Allow the spectrometer and the lamp to obtain stability and adjust the instrumental conditions for manganese analysis. Set the wavelength at 279,5 nm as described by the manufacturer.

8.1.2 Install the burner-head for acetylene-air and ignite the flame.

8.1.3 Adjust the flow rates of air (4.7) and acetylene (4.8) to obtain an oxidising flame, which should be fuel lean and light blue in colour. Aspirate the kerosene (4.1) and adjust the flow rate of kerosene to keep the flame lean and blue.

NOTE A reduced flow rate of kerosene (4.1) is employed to avoid the formation of carbon residues that can affect the stability of the flame.

8.2 Preparation of the calibration

8.2.1 Set the absorbance to zero while aspirating the kerosene (4.1).

8.2.2 Aspirate calibration solution 3 and adjust the burner position to get the maximum absorbance.

8.2.3 Set the absorbance to zero while aspirating the blank (7.2). Aspirate calibration solutions 1 to 5 (7.2) to check for linearity.

8.2.4 Aspirate calibration solutions 1 to 5 (7.2) and record the absorbance values. For each calibration solution perform three absorbance measurements with an integration time from 3 s to 5 s and calculate the mean absorbance value.

The relative standard deviation (*RSD*) of the mean absorbance values shall be lower than 3 %. Higher *RSD* indicate the presence of nebulisation problems and/or burner head dirt. In the latter case, nebulisation chamber and burner head shall be cleaned and the procedure repeated from 8.1.2.

8.2.5 A calibration curve for manganese is constructed using a linear regression with concentration of the element in the calibration solutions (7.2) as independent variable (X) and the corresponding absorbance values of manganese as dependent variable (Y) according to Equation (1):

$$Y = a \times X + b \quad (1)$$

where

a is the slope of the linear regression;

b is the intercept on Y-axis.

The construction of the calibration curve is done with use of built-in software of the spectrometer.

8.3 Check of the calibration

The calibration curves shall be checked in regular intervals. A Quality Control (QC) solution shall be prepared from certified reference materials or from certified stock solutions to verify sensitivity and accuracy of the calibration curve (7.2).

If the manganese content of the QC solution (7.2) differs from the reference value by more than R/1,41 (reproducibility divided by 1,41), prepare a new QC solution as in 7.2. If the manganese content of the new QC solution still differs from the reference value, a new calibration shall be established.