SIST

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

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

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

Carburants pour automobiles - Détermination de la teneur en manganèse dans les essences sans plomb - Méthode d'émission atomique à couplage inductif par plasma (ICP OES)

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

Carburants pour automobiles - Détermination de la teneur en manganèse dans les essences sans plomb - Méthode spectrométrique optique par plasma à couplage inductif (ICP OES)

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

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Foreword

This document (EN 16136:2011) 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of an identical text or by endorsement, at the latest by June 2012, and conflicting national standards shall be withdrawn at the latest by June 2012.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 inductively coupled plasma optical emission spectrometry (ICP OES) 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 anti-knock 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 petrol are unstable when exposed to light. Low and erratic results are expected if petrol 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 a procedure.

NOTE 4 Application of the test method to the determination of other manganese compounds in 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 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 petrol sample is diluted with a hydrocarbon solvent. The solution is introduced directly into the plasma of an ICP OES spectrometer. 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 manganese concentration below the detection limit of the instrument 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 (5.1.3) and fill to 500 ml with kerosene (4.1).

4.4 Manganese standard solution, dissolved in oil, *c*(Mn) = 100 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.

4.5 Argon, with a minimum purity of φ(Ar) ≥ 99,995 **%** (*V/V*).

NOTE Small amounts of oxygen (minimum purity $\varphi(O_2)$ ≥ 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

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 and 50 ml, according to EN ISO 1042, with taper sleeve and plug.

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

5.1.4 Graduated pipette or variable volume automatic pipettes, fitted with disposable polypropylene tips.

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

5.3.1 General

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.

NOTE A cooled spray chamber can be used, provided that the temperature is controlled +/- 1 °C.

5.3.2 Wavelengths

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

Table 1 – Recommended wavelengths

Element	Wavelength nm
Manganese	257,610
	260,569
	293,931
	259,372

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, manganese standard solution (4.4) shall be shaken vigorously before use. It is strongly advised to use freshly prepared calibration solutions.

7.2 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 (5.1.3). 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.

7.3 Preparation of the calibration solutions

The calibration solutions shall be prepared as indicated in Table 2. Each mass of manganese intermediate dilution solution (7.2) shall be weighed to the nearest 0,1 mg into a 20 ml volumetric flask (5.1.2.2). Fill with solvent (4.3) to the mark.

All solutions thus prepared shall be homogenized by shaking.

Table 2 — Concentration of manganese in the solutions

Calibration solutions	**Manganese intermediate solution** g	**Manganese concentration** mg/l
blank	0,00	0,00
1	0,10	0,05
2	0,20	0,10
3	0,40	0,20
4	1,00	0,50
5	2,00	1,00

7.4 Preparation of manganese quality control solution

A 0,10 mg/l quality control (QC) solution shall be prepared using an independent manganese standard solution.

The mass given is based on a manganese content of 100 mg/kg. In case a standard solution with different element content is used, the mass shall be adjusted accordingly to obtain the specified element content.

Weigh 0,05 g of manganese standard solution (4.4) to the nearest 0,1 mg into a 50 ml volumetric flask (5.1.2.2). Fill with solvent (4.3) to the mark.

All solutions prepared shall be homogenized by shaking.

8 Calibration

8.1 General

The ICP OES spectrometer set up and instrument check is performed according to the instructions from the manufacturer. Follow the manufacturer's instructions for setting up the instrument with organic solutions.

The choice of the instrumental parameters is determined to obtain the best signal/background ratio for manganese.

Net intensity of analytical lines shall be calculated by subtracting the intensity measured at appropriate background wavelengths. The background subtraction shall be performed at wavelengths not affected by other lines. Some instruments are equipped with software which allows the automatic correction of the background.