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BSI Standards Publication

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

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National foreword

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A list of organizations represented on this committee can be obtained on request to its secretary.

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

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

Kraftstoffe für Kraftfahrzeuge - Bestimmung des Gehaltes an Mangan und Eisen in Dieselkraftstoff - Optische Emissionsspektrometrie mit induktiv gekoppeltem Plasma (ICP OES)

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Foreword

This document (EN 16576:2014) 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of an identical text or by endorsement, at the latest by May 2015 and conflicting national standards shall be withdrawn at the latest by May 2015.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 answers requirements originating from the amended Fuels Quality Directive (FQD, [1]).

A similar technique for unleaded petrol is described in EN 16136 [2].

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1 Scope

This European Standard specifies a method based on inductively coupled plasma optical emission spectrometry (ICP OES) for the determination of manganese content and of iron content, each from about 0,5 mg/l to about 7,0 mg/l in diesel fuels including those containing up to about 10 % (*V*/*V*) fatty acid methylester (FAME).

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 and iron contents higher than 7,0 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 2 For the purposes of this European Standard, the term "% (*V*/*V*)" is used to represent the volume fraction (φ) of a material.

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 diesel fuel 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 effects.

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.

Other grades of kerosene with analyte concentrations below the detection limits for the two elements under investigation may be used. In this case, perform a wavelength check for absence of signals from the corresponding elements as well as for absence of spectral interference.

4.2 Manganese standard solution, dissolved in oil, μ(Mn) = 100 mg/kg.

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

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.

4.3 Iron standard solution, dissolved in oil, μ(Fe) = 100 mg/kg.

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

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.

4.4 Internal standard solutions (cobalt, scandium, yttrium), dissolved in oil, for example with 1 000 mg/kg per element, available as single element standards.

NOTE The element standard solutions are commonly available as single element standards with various element content.

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

Small amounts of oxygen (purity 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, 50 ml and 500 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 pipettes or variable volume automatic pipettes, fitted with disposable polypropylene tips.

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.

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 used for calculations.

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 filled into clean containers.

7 Preparation of solutions

7.1 General

In order to avoid inhomogeneity, the element standard solutions (4.2, 4.3 and 4.4) shall be shaken vigorously before use. It is strongly advised to use freshly prepared calibration solutions.

7.2 Preparation of the Internal standard solution for dilution

Weigh 5 g of cobalt, scandium or yttrium stock solution (4.4) with a precision of 0,1 g in a 500 ml volumetric flask (5.1.2.2).

Fill up to 500 ml with kerosene solvent (4.1).

The prepared solution shall be homogenized by vigorous shaking.

NOTE Experience from daily practice with yttrium used as internal standard has shown that internal standard solutions can be used for about two weeks.

Internal standard solution with different element content may be used instead of the 1 000 mg/kg one. In that case, the mass has to be adjusted in order to get a minimum content of 10 mg/l in the internal standard solution for dilution.

7.3 Preparation of the manganese intermediate solution

Weigh 3,00 g ± 0,01 g of manganese standard solution (4.2) into a 50 ml HDPE bottle (5.1.3). Add kerosene solvent (4.1) to 15,00 g ± 0,01 g. In case manganese standard solutions (4.2) with different manganese content are used, the mass of standard solution shall be adjusted accordingly to achieve 20 mg/kg manganese content.

7.4 Preparation of the iron intermediate solution

Weigh 3,00 g ± 0,01 g of iron standard solution (4.3) into a 50 ml HDPE bottle (5.1.3). Add kerosene solvent (4.1) to 15,00 g ± 0,01 g. In case iron standard solutions (4.3) with different iron content are used, the mass of standard solution shall be adjusted accordingly to achieve 20 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 solution (7.3) and iron intermediate solution (7.4) shall be weighed to the nearest 0,1 mg into a 20 ml volumetric flask (5.1.2.2). Fill with kerosene (4.1) to the mark.

All solutions thus prepared shall be homogenized by shaking.

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

Calibration solution	**Manganese intermediate solution (7.3)** g	**Iron intermediate solution (7.4)** g	**Internal standard solution (7.2)** ml	**Manganese concentration** mg/l	**Iron concentration** mg/l
Blank	0,00	0,00	10	0,00	0,00
1	0,50	0,50	10	0,50	0,50
2	2,00	2,00	10	2,00	2,00
3	3,50	3,50	10	3,50	3,50

7.6 Preparation of manganese and iron quality control solution

A 1,0 mg/l quality control (QC) solution shall be prepared using independent manganese and iron standard solutions. The mass given is based on an element (Fe, Mn) 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 0,5 g of manganese standard solution (4.2) and 0,5 g of iron standard solution (4.3) to the nearest 0,1 mg into a 50 ml volumetric flask (5.1.2.2), add 25 ml of the internal standard solution (7.2), and fill with kerosene (4.1) to the mark.

All solutions thus prepared shall be homogenized by shaking.

8 Calibration

8.1 General

The ICP OES spectrometer set up and instrument check are 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 all elements.

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.

8.2 Calibration of the ICP OES spectrometer

The calibration of the ICP OES spectrometer shall be done by the measurement of the blank solution and of the calibration solutions (7.5) using three replicates. At least one of the wavelengths recommended in Table 1 shall be used. It is important to ensure that the wavelengths used in calibration also match exactly the ones used in the sample measurement.

Depending on the spectrometer software, follow either procedure A or B.

8.3 Procedure A

For each element under investigation, conduct the aspiration of the calibration solutions (7.5).

For each calibration solution, measure the net emission intensity of iron, I_{Fe}, and of manganese, I_{Mn}, and the net emission intensity of the internal standard, I_{IS}, at the chosen wavelengths.

Calculate the intensity ratio of iron, R_{Fe}, and of manganese, R_{Mn}, of each calibration solution using the following formulae:

$$R_{\mathrm{Fe}} = \frac{I_{\mathrm{Fe}}}{I_{\mathrm{IS}}}, \tag{1}$$

$$R_{\mathrm{Mn}} = \frac{I_{Mn}}{I_{\mathrm{IS}}} \tag{2}$$

A calibration curve for iron and a calibration curve for manganese are constructed using linear regression with concentration of the element in the calibration solutions (7.5) as independent variable (X) and the corresponding mean intensity ratio R of iron or of manganese as dependent variable (Y) according to Formula (3).

$$Y = m \cdot X + b \tag{3}$$

where

m is the slope of the calibration curve;

b is the intercept.

8.4 Procedure B

Conduct the aspiration of the blank solution to measure the net emission intensity of the internal standard (I_{Blank}).

Conduct the aspiration of the each following calibration solution to measure the net emission intensity of iron I_{Fe}, of manganese I_{Mn} and of internal standard I_{IS}.

Calculate the correction factor R_c of each calibration solution using the formula:

$$R_C = \frac{I_{Blank}}{I_{IS}} \quad (4)$$

Calculate the corrected intensity of iron I_{FeCor} and of manganese I_{MnCor} of each working solution using the formulae:

$$I_{FeCor} = R_C \cdot I_{Fe} \quad (5)$$

$$I_{MnCor} = R_C \cdot I_{Mn} \quad (6)$$

A calibration curve for iron and a calibration curve for manganese are constructed using linear regression with concentration of the element in the calibration solutions (7.5) as independent variable (X) and the corrected intensity of iron or of manganese as dependent variable (Y) according to Formula (7).

$$Y = m \cdot X + b \quad (7)$$

where

m is the slope of the calibration curve;

b is the intercept.

8.5 Check of the calibration

The calibration curves shall be checked at regular intervals to verify sensitivity and accuracy of the calibration curve using a QC solution (see 7.6). If the manganese or iron content of the QC solution differs from the reference value by more than 10 %, prepare a new QC solution as in 7.6. If manganese or iron content of the new quality control solution differs from the reference value, a new calibration shall be established.

9 Sample analysis

9.1 Sample solution preparation

Homogenize the sample by vigorous shaking.

Transfer 25 ml of sample into a 50 ml volumetric flask (5.1.2.2) by means of a pipette (5.1.4).

Weigh the sample portion, m_s, to the nearest 0,1 mg using the analytical balance (5.2) and fill to the mark with the internal standard solution (7.2).

The solution shall be thoroughly homogenized by shaking.

The solutions shall be analysed just after the preparation.

9.2 Sample solution measurement

The determination of manganese and iron is performed with the same instrumental parameters and wavelengths used for the calibration of the spectrometer (8.2).

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.

Perform three measurements of the net emission intensity of manganese, I_{Mn}, of iron, I_{Fe}, and of internal standard, I_{IS}, at the chosen wavelengths and calculate the mean values.

The relative standard deviation (*RSD*) of I_{IS} shall not be higher than 3 %, otherwise that might indicate nebuliser problem. If the *RSD* of I_{IS} is higher than 3 %, check the calibration solution (7.5).

For procedure A (8.3), calculate the intensity ratio, *R,* of each element using the corresponding Formula (1) and Formula (2).

For procedure B (8.4), calculate the corrected intensity of each element using Formula (4) and the corresponding Formula (5) and Formula (6).

Allow sufficient rinsing time after each sample analysis.

The drift of the spectrometric system has to be checked before and at the end of the sample series or at least between every 10 samples using the control solution sample (7.6). If manganese or iron content of the control solution differs from the reference value by more than 10 %, proceed as indicated in 8.5.

10 Calculation

The content of manganese or iron of the diesel fuel sample is calculated from manganese or iron intensity using Formula (3) for Procedure A (8.3) and Formula (7) for Procedure B (8.4). This is done with use of the appropriate software functions of the ICP spectrometer.

The content of iron or manganese of the diesel fuel sample is calculated according to Formula (8):

$$C_{\text{Element}} = \frac{S_{\text{Element}} \times \rho \times 50}{m_s} \qquad (8)$$

where

C_{Element} is the content of element (manganese and iron) of the diesel fuel sample, expressed in mg/l;

S_{Element} is the content of element (manganese and iron) of the sample solution, expressed in mg/l;

ρ is the density of the diesel fuel sample (measured by EN ISO 12185 or EN ISO 3675 at 15 °C and corrected to the temperature at which the analysis is done), expressed in g/ml;

50 is the volume of the flask (9.1), expressed in ml;

m_S is the sample portion weight (9.1), expressed in g.

11 Expression of results

Report the manganese content and the iron content separate, each in mg/l, rounded to the nearest 0,01 mg/l.

12 Precision

12.1 General

The precision given in 12.2 and 12.3 was determined by statistical examination of interlaboratory test results in accordance with EN ISO 4259 [3].

12.2 Repeatability, *r*

The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values calculated according to the following formulae only in one case in twenty.

For manganese: $r = 0{,}035\ 2\ X + 0{,}029\ 0$ (9)

For iron: $r = 0{,}039\ 1\ X + 0{,}024\ 1$ (10)

where

X represents the mean of the two results expressed in mg/l.

12.3 Reproducibility, *R*

The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values calculated calculated according to the following formulae only in one case in twenty.

For manganese: $R = 0{,}114\ 7\ X + 0{,}094\ 4$ (11)

For iron: $R = 0{,}138\ 2\ X + 0{,}085\ 1$ (12)

where

X represents the mean of the two results expressed in mg/l.

13 Test report

The test report shall specify:

a) the reference to this European Standard, i.e. EN 16576;

b) the type and complete identification of the product tested;

c) the used method of sampling (see Clause 6);

d) the results of the test (see Clause 11);

e) all operating details not specified in this European Standard, or regarded as optional, together with details of any incidents which may have influenced the test result(s);

f) the date of the test.

Bibliography

[1] *Directive 2009/30/EC of the European Parliament and of the Council of 23 April 2009 amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions and amending Council Directive 1999/32/EC as regards the specification of fuel used by inland waterway vessels and repealing Directive 93/12/EEC*, OJ L 140, 5.6.2009, p. 88-113

[2] EN 16136, *Automotive fuels— Determination of manganese content in unleaded petrol — Inductively coupled plasma optical emission spectrometry (ICP OES) method*

[3] EN ISO 4259, *Petroleum products — Determination and application of precision data in relation to methods of test (ISO 4259)*

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