
Tekoči naftni proizvodi - Določevanje žvepla v motornem gorivu etanol (E85) - Metoda z valovno-disperzno rentgensko fluorescenčno spektrometrijo

Liquid petroleum products - Determination of the sulfur content in Ethanol (E85) automotive fuel - Wavelength dispersive X-ray fluorescence spectrometric method

Flüssige Mineralölerzeugnisse - Bestimmung des Schwefelgehalts in Ethanolkraftstoff (E85) - Wellenlängendispersives Röntgenfluoreszenz-Spektrometrie-Verfahren

Produits pétroliers liquides - Détermination de la teneur en soufre dans le carburant éthanol pour automobiles (E85) - Méthode spectrométrique par fluorescence de rayons X dispersive en longueur d'onde

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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European foreword

This document (EN 16997:2017) 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of an identical text or by endorsement, at the latest by February 2018, and conflicting national standards shall be withdrawn at the latest by February 2018.

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

The methodology described in this document is based on EN ISO 20884 [1] and EN 15485 [2].

According to the CEN-CENELEC Internal Regulations, the national standards organisations 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, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

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EN 16997:2017 (E)

1 Scope

This European Standard specifies a wavelength-dispersive X-ray fluorescence (WDXRF) test method for the determination of the sulfur content in ethanol (E85) automotive fuel [3], containing ethanol between 50 % (V/V) and 85 % (V/V), from 5 mg/kg to 20 mg/kg, using instruments with either monochromatic or polychromatic excitation.

NOTE 1 Sulfur contents higher than 20 mg/kg can be determined after sample dilution with an appropriate solvent. However, the precision was not established for diluted samples.

NOTE 2 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.

WARNING — The use of this Standard can involve hazardous materials, operations and equipment. This Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of users of this standard to take appropriate measures to ensure the safety and health of personnel prior to application of the standard, and fulfil statutory and regulatory requirements for this purpose.

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 3170, *Petroleum liquids - Manual sampling (ISO 3170)*

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

EN ISO 22854, *Liquid petroleum products - Determination of hydrocarbon types and oxygenates in automotive-motor gasoline and in ethanol (E85) automotive fuel - Multidimensional gas chromatography method (ISO 22854)*

3 Principle

The sample under analysis is exposed in a sample cell to the primary radiation of an X-ray tube. The count rates of the S K-L_{2,3} X-ray fluorescence and the count rate of the background radiation are measured. The correlation between the pulse rate and the concentration is calculated by software. The matrix effects are compensated either on the basis of fundamental parameters or using a correction table. The sulfur content is then determined using this calibration.

4 Reagents and materials

4.1 General

Compounds with a minimum purity of 99 % (m/m) as in 4.2 to 4.4. Where the purity of these compounds is less than 99 % (m/m), the concentrations and nature of all impurities shall be established.

A correction for chemical impurity may be applied when the sulfur content is known with accuracy.

Certified reference materials (CRMs) from accredited suppliers are suitable alternatives to the compounds listed in 4.2 to 4.4.

4.2 Dibutylsulfide, of nominal sulfur content 21,92 % (m/m), **or dibutyldisulfide**, of nominal sulfur content 35,95 % (m/m), used as a calibrating substance for sulfur.

4.3 Ethanol absolute, of a purity not less than 99 %, for use as a compound of the blank solution (7.2), high purity grade, with a sulfur content < 1 mg/kg.

Check the blank solution (7.2) prior to use with the spectrometer (5.1). A signal for sulfur shall not be detectable.

4.4 n-Heptane, of a purity not less than 99 %, for use as a compound of the blank solution (7.2), high purity grade, with a sulfur content < 1 mg/kg.

Check the blank solution (7.2) prior to use with the spectrometer (5.2). A signal for sulfur shall not be detectable.

5 Apparatus

5.1 Software to set up a calibration and for the application to the fundamental parameter method of calculating the corresponding correction factor for the varying ethanol content in the sample in the calibration and the in use of such a calibration during the evaluation of samples. The software can be part of the device software, separate software is also possible. If software for the application of the fundamental parameter method isn't available, the correction table (Table 3) may be used. The correction factors of Table 3 are only applicable for monochromatic excitation.

5.2 Wavelength-dispersive X-ray fluorescence spectrometer, with the capability for measuring the count rates of the S K-L_{2,3} X-ray fluorescence radiation and the background radiation. Due to the inherently low background radiation produced by instruments utilizing monochromatic radiation for excitation, it is not mandatory to measure the background radiation when this type of instrument is used. The minimum requirements for the spectrometer are given in Table 1.

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

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6 Sampling

Unless otherwise specified, laboratory samples shall be obtained by the procedures described in EN ISO 3170 or EN ISO 3171.

Samples should be analysed as soon as possible after removal from bulk supplies to prevent loss of sulfur.

Thoroughly mix samples in their containers prior to withdrawal of the test portions.

IMPORTANT — Particular attention should be paid to avoid contamination of sampling bottles from phosphorus containing detergents and thus to prevent the risk of interference with sulfur.

Table 1 — Spectrometer requirements

Component	Polychromatic excitation	Monochromatic excitation
Anode	Rhodium, scandium or chromium	Rhodium, scandium, chromium or titanium
Voltage ^a	No less than 30 kV (S) No less than 50 kV (Compton)	No less than 30 kV
Current ^a	No less than 33 mA (S) No less than 20 mA (Compton)	No less than 0,1 mA
Collimator or optic	Coarse collimator	Monochromator
Analysing crystal	Germanium, pentaerythrite or graphite LiF200 for Rh (Compton)	Germanium, pentaerythrite or graphite
Optical path ^b	Vacuum or helium	Vacuum or helium
Sample cup window ^c	Polyester film, 4 µm maximum	Polyester film, 4 µm maximum
Detector	Proportional counter with pulse-height analyser (S) Scintillation counter with pulse-height analyser (Compton)	Proportional counter with single channel analyser
Wavelengths	S K-L _{2,3} at 0,537 3 nm Background radiation at 0,545 nm Tube anode element's Compton signal ^d	S K-L _{2,3} at 0,537 3 nm

^a Lower-power systems may be used, provided they have been validated to meet the precision requirements specified in Clause 12.

^b In instruments using vacuum, the sample is not exposed directly to the vacuum of the optical path, but is separated by a secondary window. Helium, minimum purity 99,9 %.

^c Polyester film is the preferred choice as samples of very high aromatic content may dissolve polycarbonate film. There are possibly trace amounts of silicon, calcium and sulfur in some types of film. However, the effects should be cancelled out when samples and standards are analysed using the same batch of film. It is important that samples, standards and blanks be measured using the same batch of film to avoid bias. Other sample window materials with the same or better absorptivity, purity and stability can also be used.

^d As the peak position of the tube line's Compton peak also depends on the spectrometer geometry it is not possible to present the absolute position / wavelength. The peak position can be set with the blank standard 0. The Compton peak is a broad peak on the low energy / high 2 theta angle side of the tube anode's normal (Rayleigh) signal.

7 Preparation of calibration solutions

7.1 Interferences

7.1.1 Background

Differences between the elemental composition of test samples and the calibration standards can result in biased sulfur results. For samples within the scope of this test method, elements contributing to bias resulting from differences in the matrices of calibrants and test samples are hydrogen, carbon, and oxygen. Ethanol containing petrol, e.g. E85, has a high oxygen content leading to a significant absorption of S K-L_{2,3} radiation and low sulfur results.

7.1.2 FP-Method

A method for the matrix compensation is the commonly referred to fundamental parameter method (FP method) in this particular case using the Compton signal of the XRF analyser. Follow manufacturer instructions for the use of matrix correction by FP methodology. Also see Annex A for more information.

7.1.3 Correction table

If monochromatic excitation is used, the matrix compensation shall be applied using a correction table (see Table 3). A correction factor from the table is applied by multiplying the measurement results by the correction factor. The correction table (Table 3) is only valid for monochromatic excitation and calibration with the calibration matrix as defined in 7.4.

7.2 Blank calibration solution

Use a 75 % (V/V) Ethanol (4.3) and 25 % (V/V) n-Heptane (4.4) mixture as a blank solution (7.2).

7.3 Stock solution

Weigh a quantity of the required calibrating substance (4.1 or 4.2) to the nearest 0,1 mg, and dilute with blank solution (7.2) at room temperature so that a stock solution with an accurately known sulfur content (to the nearest 1 mg/kg) of approximately 1 000 mg/kg is obtained.

CAUTION — Care should be taken due to volatility of the calibrating substance.

7.4 Calibration solutions

Weigh the stock solution (7.3) to the nearest 0,1 mg into suitable containers and dilute with blank solution (7.2) so that calibration solutions with sulfur contents in accordance with Table 2 are provided by stirring at room temperature. Containers made from glass, plastic material (HDPE, FEP, PFA) and metallic epoxy containers are suitable and may be used.

The sulfur contents in the calibration solutions are indicated in milligrams per kilogram, rounded to the nearest 0,1 mg/kg.

7.5 Storage and stability of the calibration solutions

Calibration solutions prepared in accordance with Table 2 have a limited stability and shall be used on the same day they are prepared.

While stock solutions can be stable for a longer time, calibration solutions may not.

Table 2 — Calibration solutions, sulfur content in mg/kg

Number	Polychromatic Excitation	Monochromatic Excitation
0 (blank solution)	0,0	0,0
1	5,0	5,0
2	10,0	10,0
3	15,0	20,0
4	20,0	50,0
5	50,0	