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Ethanol as a blending component for petrol - Determination of sulfur content -
Wavelength dispersive X-ray fluorescence spectrometric method

Ethanol zur Verwendung als Blendkomponente in Ottokraftstoff - Bestimmung des
Schwefelgehaltes - Wellenlängendispersive Röntgenfluoreszenz-Spektrometrie (wdRFA)

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Éthanol comme base de mélange a l'essence - Dosage du soufre - Méthode de
fluorescence de rayon X dispersive en longueur d'onde

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English Version

Ethanol as a blending component for petrol - Determination of
sulfur content - Wavelength dispersive X-ray fluorescence
spectrometric method

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soufre - Méthode par fluorescence X dispersive en longueur
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Ottokraftstoff - Bestimmung des Schwefelgehaltes -
Wellenlängendispersive Röntgenfluoreszenz-Spektrometrie
(wdRFA)

This European Standard was approved by CEN on 30 June 2007.

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN Management Centre has the same status as the official versions.

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

Management Centre: rue de Stassart, 36 B-1050 Brussels

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Foreword

This document (EN 15485:2007) 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of an identical text or by endorsement, at the latest by February 2008, and conflicting national standards shall be withdrawn at the latest by February 2008.

The method described in this document is based on EN ISO 20884 [1].

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, 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 United Kingdom.

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1 Scope

This document specifies a wavelength-dispersive X-ray fluorescence (WDXRF) test method for the determination of the sulfur content of ethanol from 7 mg/kg to 20 mg/kg.

NOTE For the purposes of this European Standard, the term "% (m/m)" is used to represent the mass fraction of a material.

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

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 α X-ray fluorescence and the count rate of the background radiation are measured. The sulfur content of the sample is determined from a calibration curve defined for the relevant measuring range.

NOTE Whilst the Siegbahn X-ray line notation (S-K α) is used in this document, the corresponding IUPAC X-ray line notation is S K-L_{2,3}.

4 Reagents and materials

4.1 **Dibutylsulfide**, of nominal sulfur content 21,92 % (m/m), or

4.2 **Dibutyldisulfide**, of nominal sulfur content 35,95 % (m/m), used as a calibrating substance for sulfur.

4.3 **Ethanol absolute**, where the purity is not less than 99 %, for use as a blank solution, high purity grade, with a sulfur content < 1 mg/kg. Check the blank solution prior to use with the spectrometer (5.1). A signal for sulfur shall not be detectable.

5 Apparatus

5.1 **Wavelength dispersive X-ray fluorescence spectrometer**, with the capability for measuring the count rates of the S-K α X-ray fluorescence radiation and the background radiation. The minimum requirements for the spectrometer are given in Table 1.

Table 1 — Spectrometer requirements

Component	Requirement	Recommendations
Anode	Rhodium, scandium or chromium	
Voltage ^{a)}	No less than 30 kV	30 kV
Current ^{a)}	No less than 50 mA	100 mA
Collimator	Coarse	
Analysing crystal	Germanium, pentaerythrite, or graphite	Germanium
Optical path	Helium	
Sample cup window ^{b)}	Polyester film, sulfur-free, 4 µm maximum	Polyester film 3,5 µm
Detector	Proportional counter with pulse-height analyser	
<p>^a Lower power systems may be used, provided that these have been validated to meet the precision requirements specified in Clause 12.</p> <p>^b Other sample window materials with the same or better transparency, purity and stability, can also be used.</p>		

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

6 Samples and sampling

Unless otherwise specified, laboratory samples shall be obtained by the procedures described in EN ISO 3170. High density polyethylene containers shall be used. The containers should be carefully cleaned and rinsed with pure water to avoid contamination.

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

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

NOTE Particular attention should be paid to avoid contamination of sampling bottles from phosphorus containing detergents.

7 Preparation of calibration solutions

7.1 Blank calibration solution

Use ethanol (4.3) as a blank solution.

7.2 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 (7.1) 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.

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

7.3 Calibration solutions

Weigh the stock solution (7.2) to the nearest 0,1 mg into bottles and dilute with blank solution (7.1) so that standard solutions with sulfur contents in accordance with Table 2 are provided by stirring at room

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

Table 2 — Calibration solutions

Number	Sulfur content mg/kg
0 (blank solution)	0,0
1	5,0
2	10,0
3	20,0

7.4 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.

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

8 Settings

8.1 Measuring parameters

For optimum measuring parameters, refer to Table 1.

8.2 Optimization

The spectrometer shall be optimized in accordance with the manufacturer's specifications in order to achieve the optimum signal-to-noise ratio. The calibration solution with 20 mg/kg sulfur is recommended for optimization.

The counting time shall be adjusted such that, for the 20 mg/kg calibration solutions, an optimal signal-to-noise ratio and signal area, for example resulting from 15 000 net counts, is obtained. This optimized counting time shall be used for both calibration (see 9) and measurement (see 10).

8.3 Performance check of the spectrometer

Prior to a measurement series (calibration and/or measurement), but in any case at least once daily, the manufacturer's specifications shall be used to check that the spectrometer is operating correctly, so that an optimum performance and a consistent standard of highest possible quality is ensured.

NOTE 1 Many modern WDXRF systems use drift monitoring and correction to ensure that systems produce accurate data over long periods of time without the need to recalibrate.

NOTE 2 Performance checks should be performed on a regular basis, since such checks will give valuable information about the status and stability of the spectrometer.

9 Calibration

9.1 General

Take care to ensure that the spectrometer is in an optimized condition after having executed all provisions given in Clause 8 and operating optimally before calibration (see 8.3).

9.2 Calibration solutions

Transfer the calibration solutions (7.3) into suitable sample cups and fill them half full (see the note below). Depending on the concentration range, all calibration solutions prepared in accordance with Table 2 shall be measured consecutively in ascending order. The count rate, I_s , of the S-K α X-ray fluorescence radiation at 0,537 3 nm, and the count rate, I_B , of the background radiation at 0,545 nm, shall be measured consecutively.

NOTE Too small sample quantities will give a low result or relatively more evaporation/concentration effects when measuring volatile samples, whilst too much quantity of sample will give more sagging of the cell window especially when light aromatic samples are measured.

9.3 Calibration curves

The net count rate, I_0 , is calculated according to equation (1). To determine the calibration curve, the relevant net count rate, I_0 , is plotted against the corresponding sulfur content of the calibration solution; the calibration curve shall then be calculated and stored using the linear model according to equation (2). The regression calculation may be carried out either separately or using the spectrometer calculator.

$$I_0 = I_s - I_B \quad (1)$$

where

I_0 is the net count rate for the relevant determination;

I_s is the count rate of the S-K α X-ray fluorescence radiation at 0,537 3 nm;

I_B is the count rate of the background radiation at 0,545 nm;

$$I_0(x) = a + bx \quad (2)$$

where

x is the sulfur content of the relevant calibration solution, expressed in milligrams per kilogram (mg/kg);

a, b are the parameters from the regression calculation;

$I_0(x)$ is the net count rate computed from the regression calculation for the content, x .

9.4 Checking

Check the WDXRF system daily or before a measurement series by using quality control samples with known sulfur contents. Check immediately when using a new batch of films. If the check result differs by more than the 0,71 R , where R is the reproducibility of this test method (see 12.2), execute a recalibration.

NOTE It is recommended to execute a control chart analysis.

10 Procedure

Fill a sample cup with a sufficient quantity of the sample under analysis so that an approximate medium height level is achieved (see the note to 9.2). Expose the sample to the radiation of the X-ray tube. Measure consecutively the count rate, I_s , of the S-K α X-ray fluorescence radiation at 0,537 3 nm and the count rate, I_B , of the background radiation at 0,545 nm.

Calculate the net count rate, I_0 , according to equation (1). Read the sulfur content in milligrams per kilogram from the calibration curve (see 9.3) for the measuring range of 7 mg/kg to 20 mg/kg sulfur. If the sulfur content