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Petroleum products — Determination of sulfur content of automotive fuels — Wavelength-dispersive X-ray fluorescence spectrometry

Produits pétroliers — Détermination de la teneur en soufre des carburants pour automobiles — Spectrométrie de fluorescence de rayons X dispersive en longueur d'onde

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 28, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*.

This third edition cancels and replaces the second edition (ISO 20884:2011), which has been technically revised. The main changes compared to the previous edition are as follows:

- extension of the scope to include hydrotreated vegetable oil (HVO) and the synthetic fuel “gas to liquid” (GTL);
- inclusion of specific procedural steps for instruments utilizing monochromatic excitation.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Petroleum products — Determination of sulfur content of automotive fuels — Wavelength-dispersive X-ray fluorescence spectrometry

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

1 Scope

This document specifies a wavelength-dispersive X-ray fluorescence (WDXRF) test method for the determination of the sulfur content of liquid, homogeneous automotive fuels from 5 mg/kg to 500 mg/kg, which have a maximum oxygen content of 3,7 % (*m*/*m*). This product range covers:

- diesel fuels containing up to about 30 % (*V*/*V*) fatty acid methyl esters (FAME),
- motor gasolines containing up to about 10 % (*V*/*V*) ethanol,
- synthetic fuels such as hydrotreated vegetable oil (HVO) and gas to liquid (GTL) having sulfur contents in the range of 5 mg/kg to 45 mg/kg.

Products with higher oxygen content show significant matrix effects, e.g. pure FAME used as biodiesel, nevertheless, pure FAME can be analysed when the corresponding procedures are followed (see 5.3 and 8.1).

Other products can be analysed with this test method, though precision data for products other than those mentioned have not been established for this document.

NOTE 1 Sulfur contents higher than 500 mg/kg can be determined after sample dilution, however, the precision was not established for diluted samples.

NOTE 2 For the purposes of this document, "% (*m*/*m*)" and "% (*V*/*V*)" are used to represent the mass fraction, w, and the volume fraction, φ, of a material respectively.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

ISO 3170, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

4 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, where required, 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 The IUPAC X-ray line notation (S K-$L_{2,3}$) is used in this document; the corresponding Siegbahn X-ray line notation (S Kα or S $K\alpha_{1,2}$) is being phased out.

5 Reagents

5.1 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.

Care should be taken due to volatility (see Annex A for further guidance).

NOTE Certified reference materials (CRM) produced in accordance with ISO 17034[3] are suitable alternatives.

5.2 White oil (paraffinum perliquidum), for use as a blank solution, of high purity grade, with a sulfur content of less than 1 mg/kg. Check the blank solution prior to use with the spectrometer (6.1). A signal for sulfur shall not be detectable.

5.3 Methyl oleate, for use as a blank solution when pure FAME is analysed, with a sulfur content of less than 1 mg/kg. Check the blank solution prior to use with the spectrometer (6.1). A signal for sulfur shall not be detectable (i.e. the intensity shall be lower that the intensity equivalent to 1 mg/kg). Other oxygen-containing and sulfur-free blank solutions, such as octanol, can also be used.

6 Apparatus

6.1 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.

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

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	No less than 30 kV
Current[a]	No less than 50 mA	No less than 0,1 mA

[a] Lower-power polychromatic systems may be used, provided they have been validated to meet the precision values specified in Clause 13.

[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.

[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.

Table 1 *(continued)*

Component	Polychromatic excitation	Monochromatic excitation
Collimator or optic	Coarse collimator	Monochromator
Analysing crystal	Germanium, pentaerythrite or graphite	Germanium, pentaerythrite or graphite
Optical path[b]	Vacuum or helium	Vacuum or helium
Sample cup window[c]	Polyester film, 4 µm maximum thickness	Polyester film, 4 µm maximum thickness
Detector	Proportional counter with pulse-height analyser	Proportional counter with single channel analyser
Wavelengths	S K-$L_{2,3}$ at 0,537 3 nm Background radiation at 0,545 nm	S K-$L_{2,3}$ at 0,537 3 nm

[a] Lower-power polychromatic systems may be used, provided they have been validated to meet the precision values specified in Clause 13.

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7 Sampling

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

8 Calibration solutions

8.1 Blank solution

Use white oil (5.2) as a blank solution.

If pure FAME is under analysis, use a blank solution in accordance with 5.3 to minimize potential matrix effects.

8.2 Stock solution

Weigh a quantity of the required calibrating substance (5.1) to the nearest 0,1 mg, and dilute with blank solution (5.2 or 5.3, as appropriate) 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.

Care should be taken due to volatility of the calibrating substance (see Annex A for further guidance).

8.3 Calibration solutions

Weigh an appropriate quantity of the stock solution (8.2) to the nearest 0,1 mg into bottles and dilute with blank solution (5.2 or 5.3, as appropriate) so that standard solutions with sulfur contents in accordance with Tables 2 and 3 are obtained 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 — Low sulfur range

Number	Sulfur content mg/kg
Blank solution 0	0,0
2.1	5,0

Table 2 *(continued)*

Number	Sulfur content mg/kg
2.2	10,0
2.3	25,0
2.4	50,0

Table 3 — Calibration solutions — High sulfur range

Number	Sulfur content mg/kg
Blank solution 0	0,0
3.1	50,0
3.2	100,0
3.3	200,0
3.4	350,0
3.5	500,0

8.4 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 day they are prepared.

Calibration solutions prepared in accordance with Table 3 have a stability of no more than one week if stored in a cool location (refrigerator).

9 Settings

9.1 Measuring parameters

For optimum measuring parameters, refer to Table 1.

9.2 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 50 mg/kg sulfur is recommended for optimization.

For polychromatic excitation, the counting time shall be set so that the total net count from a 50 mg/kg solution is ≥ 40 000. This counting time shall be used for both calibration (see Clause 10) and measurement (see Clause 11).

For monochromatic excitation, check the manufacturer recommendation for optimization.

9.3 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.

Performance checks should be carried out on a regular basis, since such checks give valuable information about the status and stability of the spectrometer.

10 Calibration

10.1 General

Ensure that the spectrometer is in an optimized condition after having executed all provisions given in Clause 9 and operating optimally before calibration (see 9.3).

For the range from 5 mg/kg to 60 mg/kg sulfur, and for the range 60 mg/kg to 500 mg/kg sulfur, separate calibrations shall be conducted.

10.2 Calibration solutions

Transfer the calibration solutions (8.3) into suitable sample cups so that the minimum volume is achieved (see paragraph below). Depending on the concentration range, all calibration solutions prepared in accordance with Tables 2 or 3 shall be measured consecutively in ascending order. The count rate, I_S, of the S K-$L_{2,3}$ 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. For instruments utilizing monochromatic excitation, measurement of the background radiation is not required (see 6.1).

Sample quantities that are too small give a low result or relatively more evaporation/concentration effects when measuring volatile samples, while too much sample causes more sagging of the cell window, especially when aromatic samples are measured. It is necessary to determine the minimum volume by proceeding as follows: start with 1 ml, measure the net count rate, add liquid, measure again the count rate. Repeat until the count rate remains constant for greater volumes of liquid. Plot a curve of net count rate vs volume and choose a volume greater than the point at which the curve becomes flat.

For polychromatic excitation, typically use 5 g of materials in a 28 mm sample cup or 10 g of materials in a 40 mm sample cup. For monochromatic excitation, typically use 0,8 g of materials in a 20 mm sample cup and 4 g of materials in a 42,9 mm sample cup. If in doubt, check the manufacturer recommendations.

10.3 Calibration curves

The net count rate, R_0, is calculated according to Formula (1) or (2). To determine the calibration, the net count rate, R_0, is plotted as a function of the corresponding sulfur content. Use the spectrometer software or a spreadsheet program to perform a regression of the data to fit to Formula (3).

The regression calculation may be carried out either separately or using the spectrometer calculator.

$$R_0 = I_S - I_B \text{ when background is measured, or} \quad (1)$$

$$R_0 = I_S \text{ for monochromatic excitation, when no background is measured} \quad (2)$$

$$x = a + b\,R_0 + c\,R_0^2 \quad (3)$$

where

R_0 is the net count rate for the relevant determination;

I_S is the count rate of the S K-$L_{2,3}$ X-ray fluorescence radiation at 0,537 3 nm;

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

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

a, b, c are the parameters from the regression calculation.

NOTE Parameter c can be zero where the calibration curve has been shown to be linear.

10.4 Checking

Check at least two points on each calibration curve regularly, but not less frequently than every six months. It is highly recommended that quality control samples be used, with known sulfur contents for these checks. Check immediately when using a new batch of films. If the check result differs from the curve, execute a new calibration. Control limits are established from the laboratory statistical control charts, but initial values should be set before experience is established. Limits of the repeatability of this document, or 0,7 times the reproducibility, are reasonable starting points. In case of suspected changes in the equipment status (e.g. drift), recalibration is required.

11 Procedure

CAUTION — Some samples such as process rundown streams can contain finely dispersed iron sulfide which can drop onto the cell window, giving erroneously high results. In such cases, it is recommended that the samples be filtered through a 0,2 µm membrane filter prior to analysis.

11.1 Samples with sulfur contents between 5 mg/kg and 60 mg/kg

Fill a sample cup with a sufficient quantity of the sample under analysis so that the minimum volume determined in 10.2 is achieved. Expose the sample to the radiation of the X-ray tube.

Measure consecutively the count rate, $I_{S,}$ of the S K-$L_{2,3}$ X-ray fluorescence radiation at 0,537 3 nm and the count rate, I_B, of the background radiation at 0,545 nm. For instruments utilizing monochromatic excitation, measurement of the background radiation is not required (see 6.1).

Calculate the net count rate, R_0, according to Formula (1) or (2).

Read the sulfur content, in milligrams per kilogram, from the calibration curve (see 10.3) for the measuring range of 5 mg/kg to 60 mg/kg sulfur. If the sulfur content is higher than 60 mg/kg, a new sample in a new cup shall be measured using the calibration curve for the measuring range from 60 mg/kg to 500 mg/kg.

If the calibration curves were constructed using the same operation conditions, the result can be recalculated rather than re-measured.

11.2 Samples with sulfur contents between 60 mg/kg and 500 mg/kg

Fill a sample cup with a sufficient quantity of the sample under analysis so that the minimum volume determined in 10.2 is achieved.

Expose the sample to the radiation of the X-ray tube.

Measure consecutively the count rate, I_S, of the S K-$L_{2,3}$ X-ray fluorescence radiation at 0,537 3 nm and the count rate, I_B, of the background radiation at 0,545 nm. For instruments utilizing monochromatic excitation, measurement of the background radiation is not required (see 6.1).

Calculate the net count rate, R_0, according to Formula (1) or (2).

Read the sulfur content, in milligrams per kilogram, from the calibration curve (see 10.3) for the measuring range of 60 mg/kg to 500 mg/kg sulfur. If the sulfur content is higher than 500 mg/kg, the sample shall be measured using another suitable method (for instance ISO 14596[2]).

NOTE Sulfur contents higher than 500 mg/kg can be determined after sample dilution. However, the precision was not established for diluted samples.

12 Expression of results

Report the sulfur content of the sample to the nearest 0,1 mg/kg between 5 mg/kg and 99 mg/kg, and to the nearest 1 mg/kg between 100 mg/kg and 500 mg/kg.

13 Precision

13.1 General

The precision, as determined by statistical examination in accordance with ISO 4259:2006[1], is given in 13.2 and 13.3. Precision has been derived in two studies[4].

The precision for monochromatic excitation instruments (6.1) is only determined for sulfur contents from 5 mg/kg to 60 mg/kg.

13.2 Repeatability, *r*

The difference between two independent results obtained in the normal and correct operation of the same method, for test material considered to be the same, within a short interval of time, under the same test conditions, that is expected to be exceeded with a probability of 5 % due to random variation, is given in Table 4.

13.3 Reproducibility, *R*

The difference between two independent results obtained in the normal and correct operation of the same method, for test material considered to be the same, under different test conditions, that is expected to be exceeded with a probability of 5 % due to random variation, is given in Table 4.

Table 4 — Precision data

Sulfur content mg/kg	**Repeatability**, *r* mg/kg	**Reproducibility**, *R* mg/kg
5 to 60	1,7 + 0,024 8 *X*	1,9 + 0,120 1 *X*
> 60 to 500	4,0	4,6 + 0,075 *X*

NOTE 1 *X* is the average of the results being compared, in milligrams per kilogram.

NOTE 2 Precision for HVO and GTL applies only between 5 mg/kg and 45 mg/kg.

NOTE 3 Individual precision data for both polychromatic and monochromatic excitation from the 2016 interlaboratory study (ILS) are available (see Reference [4].)

14 Test report

The test report shall contain at least the following information:

a) a reference to this document (i.e. ISO 20884:2019);

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

c) the result of the test (see Clause 12);

d) any deviation, by agreement or otherwise, from the procedure specified;

e) the date of the test.

Annex A
(informative)

Good practices

A.1 Samples that contain finely divided free water or dirt can cause erroneous results. For this reason, samples that are not completely bright and clear should be filtered through a folded filter paper (Schleicher & Schuell 595 1/2[1]) or a comparable type) to remove the free water and/or dirt.

A.2 Oil from fingerprints can affect the reading when low levels of sulfur are analysed. Touching the inside of the sample cell or the portion of the window film of the cell that is exposed to X-rays should be avoided.

A.3 The sample cups should be prepared on a clean surface.

A.4 Sample cup windows should be checked for leaks and to avoid wrinkles in the film.

A.5 Sample cups containing volatile products should be covered to minimize evaporation/concentration effects.

A.6 Measurement of (many) volatile samples can affect the sensitivity of the instrument in a negative way. Checking according to 9.3 is recommended.

A.7 Sample cups already measured should not be measured again, as results that are too high can be expected. Measurement times that are too long can have the same effect.

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1) Example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

Bibliography

[1] ISO 4259:2006[2], *Petroleum products — Determination and application of precision data in relation to methods of test*

[2] ISO 14596, *Petroleum products — Determination of sulfur content — Wavelength-dispersive X-ray fluorescence spectrometry*

[3] ISO 17034, *General requirements for the competence of reference material producers*

[4] RRT-2016-701, Test methods for the determination of sulfur content in new types of marketed fuels, Report, available from the CEN/TC 19 Secretariat, NEN, PO Box 5059, 2600 GB Delft, the Netherlands, energy@nen.nl

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[2] Now withdrawn and replaced by ISO 4259 (all parts).

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