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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

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 20884 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

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

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard 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 2,7 % (*m/m*). This product range covers diesel fuels containing up to 5 % (*V/V*) fatty acid methyl ester (FAME) and motor gasolines.

Products with higher oxygen content show significant matrix effects, e.g. FAME used as biodiesel. Nevertheless, FAME may be analysed when the corresponding procedures are followed (see 4.3 and 7.1). For further details due to matrix effects and interferences, see Annex A.

Other products may be analysed with this test method. However, precision data for products other than those mentioned have not been established for this International Standard.

NOTE For the purposes of this International Standard, the terms "% (*m/m*)" and "% (*V/V*)" are used to represent the mass fraction and the volume fraction 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.

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

ISO 3171:1988, *Petroleum liquids — Automatic pipeline sampling*

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-Kα 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-Kα) is used in this International Standard, the corresponding IUPAC X-ray line notation is S K-$L_{2,3}$.

4 Reagents

4.1 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 to be taken due to volatility (see Annex A).

4.2 White oil (paraffinum perliquidum), for use as a blank solution, of 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.

4.3 Methyl oleate, for use as a blank solution when FAME is analysed, 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. Other oxygen-containing and sulfur-free blank solutions, such as octanol, can also be used.

5 Apparatus

5.1 Wavelength dispersive X-ray fluorescence spectrometer, with the capability for measuring the count rates of the S-Kα 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	

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

b Other sample window materials with the same or better transparency, purity and stability, can also be used.

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

6 Sampling

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

7 Calibration solutions

7.1 Blank solution

Use white oil (4.2) as a blank solution.

If FAME is under analysis, use a blank solution in accordance with 4.3 to minimize potential matrix effects (see Annex A).

7.2 Stock solution

Weigh a quantity of the required calibrating substance (4.1) to the nearest 0,1 mg, and dilute with blank solution (4.2 or 4.3, 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).

7.3 Calibration solutions

Weigh the stock solution (7.2) to the nearest 0,1 mg into bottles and dilute with blank solution (4.2 or 4.3) so that standard solutions with sulfur contents in accordance with Tables 2 and 3 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 — Low sulfur range

Number	Sulfur content mg/kg
Blank solution 0	0,0
2,1	5,0
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

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.

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

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 50 mg/kg sulfur is recommended for optimization.

The counting time shall be adjusted such that, for the 50 mg/kg calibration solutions, an optimal signal-to-noise ratio and signal area, for example resulting from 40 000 counts, is obtained. This optimized counting time shall be used for both calibration (see Clause 9) and measurement (see Clause 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.

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).

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.

9.2 Calibration solutions

Transfer the calibration solutions (7.3) into suitable sample cups so that an approximate medium height level is achieved (see the note 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-Kα 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 Sample quantities that are too small will give a low result or relatively more evaporation/concentration effects when measuring volatile samples, whilst too much sample will cause more sagging of the cell window, especially when light aromatic samples are measured.

9.3 Calibration curves

The net count rate, R_0, is calculated according to Equation (1). To determine the two calibration curves, the relevant net count rate, R_0, is plotted against the corresponding sulfur content of the calibration solution; the two calibration curves shall then be calculated and stored using the square model according to Equation (2). The regression calculation may be carried out either separately or using the spectrometer calculator.

$$R_0 = I_S - I_B \qquad (1)$$

$$R_0(x) = a + bx + cx^2 \quad (2)$$

where

R_0 is the net count rate for the relevant determination;

I_S is the count rate of the S-Kα 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;

$R_0(x)$ is the net count rate computed from the regression calculation for the content, x.

9.4 Checking

Check at least two points on each calibration curve regularly, but not less frequently than every six months. It is highly recommended to use quality control samples with known sulfur contents for these checks. Check immediately when using a new batch of films. If the check result differs from the curve by more than the repeatability of this International Standard, execute a new calibration. In the case of suspected changes in the equipment status (e.g. drift), recalibration is required.

10 Procedure

10.1 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 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-Kα 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, R_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 5 mg/kg to 60 mg/kg sulfur. If the sulfur content is higher than 60 mg/kg, then 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.

10.2 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 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-Kα 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, R_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 60 mg/kg to 500 mg/kg sulfur. If the sulfur content is higher than 500 mg/kg, then the sample shall be measured using another suitable method (ISO 14596, [3] and [4] in the Bibliography).

11 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.