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

Produits pétroliers — Détermination de la teneur en soufre — Spectrométrie de fluorescence 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 14596 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

This second edition cancels and replaces the first edition (ISO 14596:1998), which has been technically revised. It also incorporates the Technical Corrigendum ISO 14596:1998/Cor. 1:1999.

INTERNATIONAL STANDARD **ISO 14596:2007(E)**

Petroleum products — Determination of sulfur content — 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 method for the determination of the sulfur content of liquid petroleum products, additives for petroleum products, and semi-solid and solid petroleum products that are either liquefied by moderate heating or soluble in organic solvents (see 4.1) of negligible or accurately known sulfur content. The method is applicable to products or additives having sulfur contents in the range 0,001 % (m/m) to 2,50 % (m/m); higher contents can be determined by appropriate dilution. Other elements do not interfere at concentrations anticipated in the materials subject to this analysis.

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

High concentrations of phosphorus or chlorine [typically above 3 % (m/m)] can cause bias in the sulfur result by absorbing Zr-Lα and S-Kα to different extents. It is necessary in these cases to carry out studies to determine whether this potential interference is significant.

When larger amounts of molybdenum are present (typically above 50 mg/kg to 100 mg/kg), increased background radiation and spectral overlap with the sulfur signal can occur. It is necessary in these cases to inspect the relevant spectral regions, for example, to investigate the significance of this potential source of bias.

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 test portion and a zirconium solution as internal standard are mixed in a given mass ratio and exposed, in a sample cell, to the primary radiation of an X-ray tube.

The count rates of the S-Kα at 0,537 3 nm and Zr-Lα1 at 0,607 0 nm fluorescence thus excited and the count rate of the background radiation at 0,545 nm are measured and the ratio of these net count rates calculated. The sulfur content of the sample is determined from a calibration curve prepared on the basis of sulfur calibration standards.

NOTE 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 and materials

4.1 White oil (light paraffin oil, paraffinum perliquidum), high-purity grade, sulfur content 1 mg/kg maximum.

4.2 Sulfur compounds, of sulfur content accurately known to the nearest 0,01 % (*m*/*m*), used for the preparation of the primary standards.

The compounds given in 4.2.1 to 4.2.3 are suitable, and their nominal sulfur contents are given. Where the purity of these compounds is less than 99 %, certified materials are required, or the nature of all impurities and their contents should be accurately known to the nearest 0,01 % (*m*/*m*).

4.2.1 Dibenzothiophene (DBT), with a nominal sulfur content of 17,399 % (*m*/*m*).

4.2.2 Dibutyl sulfide (DBS), with a nominal sulfur content of 21,915 % (*m*/*m*).

4.2.3 Thionaphthene (benzothiophene) (TNA), with a nominal sulfur content of 23,890 % (*m*/*m*).

4.3 Certified sulfur reference materials.

Use materials from a national standards body or accredited suppliers, if available.

4.4 Zirconium solution A.

Zirconium octoate solution with a zirconium content in the range of 12 % (*m*/*m*) to 18 % (*m*/*m*) or another oil-soluble, sulfur-free zirconium compound dissolved in white oil (4.1) to provide a zirconium mass fraction in the range of 12 % (*m*/*m*) to 18 % (*m*/*m*).

4.5 Zirconium solution B.

Dissolve the zirconium solution A (4.4) with white oil (4.1) to provide a zirconium mass fraction of approximately 1 % (*m*/*m*).

5 Apparatus

5.1 Wavelength-dispersive X-ray fluorescence (WDXRF) spectrometer, consisting of any suitable spectrometer that incorporates the design features listed in Table 1. It shall be set up according to the manufacturer's instructions.

Table 1 — General requirements of spectrometer

Component	Requirement
Anode	Rhodium, scandium or chromium target
Voltage [a]	30 kV to 50 kV
Current [a]	30 mA to 70 mA
Collimator	Coarse
Analysing crystal	Germanium, pentaerythritol, or graphite
Optical path	Helium
Cell window	Polyester or polypropylene film, sulfur-free, thickness 2 µm to 6 µm
Detector	Gas-flow proportional counter with a pulse-height analyser

[a] A lower-power system may be used, provided that it has been validated to meet the requirements specified in 8.3 and Clause 12.

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

5.3 **Homogenizer,** non-aerating, high-speed shear type, or **heatable magnetic stirrer** or, for example, an **ultrasonic stirrer**.

5.4 **Flasks**, 50 ml capacity, narrow-necked, conical, made of borosilicate glass and fitted with a ground-glass stopper. Use flasks of higher capacity for stock solutions (7.2).

6 Samples and sampling

6.1 Unless otherwise specified, samples shall be taken in accordance with the procedure described in ISO 3170 or ISO 3171.

6.2 Test portions from the samples shall be drawn after thorough mixing and subdivision. Heat viscous samples to a temperature that renders the sample liquid and homogenize, using the homogenizer (5.3) as necessary.

NOTE For the purpose of this procedure, the term “sample” also includes solutions prepared from additives, semi-solid or solid petroleum products that have been appropriately pre-treated and/or diluted.

7 Calibration solutions

7.1 General

Use either certified reference materials (4.3) or primary standards prepared from sulfur compounds (4.2) dissolved in white oil (4.1) as a basis for the preparation of the appropriate range of sulfur stock solutions.

7.2 Preparation of stock solutions

Weigh, to the nearest 0,1 mg, a quantity of sulfur compound (4.2) or certified reference material (4.3) to prepare stock solutions of approximately 2,50 % (m/m) and 0,10 % (m/m) sulfur content, calculated to the nearest 0,001 % (m/m), and dissolve in white oil (4.1) at room temperature. Mix the contents thoroughly using a homogenizer (5.3).

The approximate quantities of sulfur compounds (4.2) for addition to 100 g of white oil (4.1) to prepare the stock solutions are as follows:

- DBT (4.2.1): 16,75 g [2,5 % (*m*/*m*)] and 0,5 g [0,1 % (*m*/*m*)]
- DBS (4.2.2): 12,85 g [2,5 % (*m*/*m*)] and 0,45 g [0,1 % (*m*/*m*)]
- TNA (4.2.3): 11,65 g [2,5 % (*m*/*m*)] and 0,40 g [0,1 % (*m*/*m*)]

It is recommended that a polytetrafluoroethylene or glass-coated magnetic stirrer and stirring device be used to mix the contents of the flask.

Calculate the exact sulfur content, $w_{\mathrm{S},2}$, as a percentage by mass, to three decimal places, in each case from the amounts of white oil and sulfur compound used as given in Equation (1):

$$w_{\mathrm{S},2} = \frac{m_\mathrm{C} \times w_{\mathrm{S},1}}{m_\mathrm{C} + m_\mathrm{O}} \qquad (1)$$

where

m_C is the mass of the sulfur compound, expressed in grams;

$w_{\mathrm{S},1}$ is the sulfur content of the sulfur compound, expressed as a percentage by mass;

m_O is the mass of white oil, expressed in grams.

7.3 Preparation of standard solutions

7.3.1 High range [0,1 % (*m*/*m*) to 2,5 % (*m*/*m*)]

Into 50 ml flasks (5.4), weigh to the nearest 0,1 mg, the appropriate quantity of the 2,5 % (*m*/*m*) stock solution (7.2) to produce approximately 25 g of each standard solution of sulfur contents approximately 2,0 % (*m*/*m*), 1,5 % (*m*/*m*), 1,0 % (*m*/*m*), 0,7 % (*m*/*m*), and 0,4 % (*m*/*m*). Add white oil (4.1) to make up to approximately 25 g and re-weigh to the nearest 0,1 mg. Calculate the sulfur content, $w_{\mathrm{S},3}$, of the standard solution to the nearest 0,001 % (*m*/*m*), using Equation (2):

$$w_{\mathrm{S},3} = \frac{(m_2 - m_1) w_{\mathrm{S},2}}{m_3 - m_1} \qquad (2)$$

where

m_1 is the mass of the flask, expressed in grams;

m_2 is the mass of the flask plus stock solution, expressed in grams;

m_3 is the mass of the flask plus stock solution plus white oil, expressed in grams;

$w_{\mathrm{S},2}$ is the sulfur content of the stock solution, expressed as a percentage by mass.

7.3.2 Low range [0,001 0 % (*m*/*m*) to 0,1 % (*m*/*m*)]

Prepare standard solutions in the same manner as described in 7.3.1 using the 0,1 % (*m*/*m*) stock solution (7.2) to give standard solutions of approximately 0,075 % (*m*/*m*), 0,05 % (*m*/*m*), 0,025 % (*m*/*m*), 0,010 % (*m*/*m*), 0,005 % (*m*/*m*) and 0,001 % (*m*/*m*). Calculate the sulfur content to the nearest 0,000 1 % (*m*/*m*) using the Equation (2).

7.4 Preparation of calibration solutions

7.4.1 High range [0,1 % (*m*/*m*) to 2,5 % (*m*/*m*)]

Weigh 20,00 g ± 0,01 g of each of the standard solutions (7.3.1) and the two stock solutions (7.2) into separate flasks (5.4), and add 5,00 g ± 0,01 g of the zirconium solution A (4.4). Mix thoroughly at room temperature (18 °C to 28 °C) using a homogenizer (5.3).

7.4.2 Low range [0,001 0 % (*m*/*m*) to 0,1 % (*m*/*m*)]

Weigh 20,00 g ± 0,01 g of the low sulfur stock solution and each of the standard solutions (7.3.2) into separate flasks (5.4) and add 2,00 g ± 0,01 g of the zirconium solution B (4.5). Mix thoroughly at room temperature (18 °C to 28 °C) using a homogenizer (5.3).

7.5 Storage of standards

Store certified reference standards in accordance with the instructions of the certifying organization, and use within the timeframe specified.

Store standards prepared from white oil and sulfur compounds in dark glass-stoppered bottles in a cool dark place.

NOTE The stability of prepared standards, under the above storage conditions, is at least six months.

8 Calibration

8.1 General

After the spectrometer has been set up and checked (5.1), purge the optical path thoroughly with helium.

8.2 High-range calibration curve [0,1 % (*m*/*m*) to 2,5 % (*m*/*m*)]

Transfer each of the calibration solutions (7.4.1) to a sample cell, and in a sequence of increasing sulfur content, place them in the spectrometer for exposure to the primary radiation.

Measure the count rates, I_{S} and I_{Zr}, of the excited S-Kα (0,537 3 nm) and Zr-Lα1 (0,607 0 nm) fluorescence radiation.

Calculate the gross count ratio, R, using Equation (3). To determine the calibration curve, the relevant gross count ratio, R, 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 (4). The regression calculation may be carried out either separately or using the spectrometer calculator.

$$R = \frac{I_{\mathrm{S}}}{I_{\mathrm{Zr}}} \tag{3}$$

$$R(x) = \mathrm{a} + \mathrm{b}x \tag{4}$$

where

R is the gross count ratio for the relevant determination;

I_{S} is the count rate of the S-Kα X-ray fluorescence radiation at 0,537 3 nm;

I_{Zr} is the count rate of the Zr-Lα1 X-ray fluorescence radiation at 0,607 0 nm;

x is the sulfur content of the relevant calibration solution, expressed as a percentage by mass;

a, b are the parameters from the regression calculation;

$R(x)$ is the gross count ratio computed from the regression calculation for the content, x.

8.3 Low-range calibration curve [0,001 0 % (m/m) to 0,1 % (m/m)]

Proceed as in 8.2 using the low range calibration solutions (7.4.2), and also measure the background radiation, I_B, at 0,545 nm. As the fluorescence radiation is diminished by the sample cell window (see Table 1), a thin film of approximately 2 µm thickness (polyester) or approximately 4 µm thickness (polypropylene) shall be used for the calibration solutions and test portions (9.2) of low sulfur content. The setting of the spectrometer shall be such that at least 50 000 counts are counted for the Zr-Lα1 line over the total measurement period.

Calculate the net count ratio, R_0, using Equation (5). To determine the calibration curve, the relevant net count ratio, R_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 (6). The regression calculation may be carried out either separately or using the spectrometer calculator.

$$R_0 = \frac{I_S - I_B}{I_{Zr} - I_B} \tag{5}$$

$$R_0(x) = \mathrm{a} + \mathrm{b}x \tag{6}$$

where

R_0 is the net count ratio for the relevant determination;

I_S is the count rate of the S-Kα X-ray fluorescence radiation at 0,537 3 nm;

I_{Zr} is the count rate of the Zr-Lα1 X-ray fluorescence radiation at 0,607 0 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 as a percentage by mass;

a, b are the parameters from the regression calculation;

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

8.4 Checking

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 requirement to recalibrate.

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

Check the calibration curves regularly. In regular use, check at least two points on each calibration curve by using quality control samples with known sulfur contents not less frequently than every three months. Check immediately when using a new batch of films. If the check result differs by more than 0,71 of the reproducibility given in this International Standard (see 12.2), execute a recalibration.

It is recommended that a control chart analysis be carried out.

9 Procedure

9.1 General

For some products, e.g. residual oils, it can be necessary to deviate from the provisions given in 9.2 and 9.3, that is, to increase the maximum temperature from 100 °C to 120 °C in order to obtain a homogenous sample. In these cases, this deviation shall be mentioned in the test report (Clause 13, item e).

9.2 Samples with sulfur contents between 0,1 % (m/m) and 2,5 % (m/m)

Weigh 20,00 g ± 0,01 g of the sample for analysis (see Note in Clause 6) into a flask (5.4) and add 5,00 g ± 0,01 g of the zirconium solution A (4.4). Homogenize thoroughly, with heating if necessary, to a maximum temperature of 80 °C. After cooling to 18 °C to 28 °C, proceed in accordance with 8.2 and calculate the gross count ratio, R.

9.3 Samples with sulfur contents between 0,001 0 % (m/m) and 0,1 % (m/m)

Weigh 20,00 g ± 0,01 g of the sample to be analysed (see Note in Clause 6) into a flask (5.4) and add 2,00 g ± 0,01 g of the zirconium solution B (4.5). Homogenize thoroughly, with heating if necessary, to a maximum temperature of 80 °C. After cooling to 18 °C to 28 °C, proceed in accordance with 8.3 and calculate the net count ratio, R_0.

10 Calculation

Read the sulfur content from the calibration curves constructed in 8.2 or 8.3. If the sulfur content is above 2,5 % (m/m), dilute the sample with white oil (4.1) and repeat the procedure specified in 9.2.

NOTE Many modern instruments contain a microprocessor that retains the calibration curve and produces a digital readout.

11 Expression of results

Report the sulfur content, as a percentage by mass, rounded to the nearest 0,000 1 % (m/m) between 0,001 0 % (m/m) and 0,009 9 % (m/m), to the nearest 0,000 1 % (m/m) between 0,010 0 % (m/m) and 0,099 9 % (m/m), and to the nearest 0,01 % (m/m) between 0,10 % (m/m) and 2,50 % (m/m).

12 Precision

12.1 Repeatability

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 given in Table 2 in only one case in twenty.

12.2 Reproducibility

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 given in Table 2 in only one case in twenty.

Table 2 — Precision data

Sulfur content % (m/m)	**Repeatability limit**	**Reproducibility limit**
0,001 0 to 0,002 9	0,000 3	0,000 5
0,003 0 to 0,004 9	0,000 6	0,001 0
0,005 0 to 0,009 9	0,001 0	0,002 0
0,010 0 to 0,029 9	0,002	0,003
0,030 0 to 0,049 9	0,003	0,005
0,050 0 to 0,099 9	0,005	0,010
0,10 to 0,99	0,01	0,02
1,00 to 2,50	0,02	0,04

13 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard (ISO 14596:2007);

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

c) the sampling procedure used (see Clause 6);

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

e) any deviation, by agreement or otherwise, from the procedure specified (e.g. see 9.1);

f) the date of the test.

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