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STANDARD

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14596

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

Produits pétroliers — Dosage du soufre — Spectrométrie de fluorescence X dispersive en longueur d'onde

Reference numbe
ISO 14596:1998(E)

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.

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.

International Standard ISO 14596 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants.*

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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 may be determined by appropriate dilution. Other elements do not interfere at concentrations anticipated in the materials subject to this analysis.

NOTE 1 For the purposes of this International Standard, the term "% (*m/m*)" is used to represent the mass fraction.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3170:1988, *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-K_α at 0,537 3 nm and Zr-$L_{\alpha 1}$ 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.

4 Reagents and materials

4.1 White oil (light paraffin oil), 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.

NOTE 2 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 concentrations should be accurately known to the nearest 0,01 % (*m/m*).

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

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

4.2.3 Thionaphthene (Benzothiophene)(TNA), nominal sulfur content 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 zirconium compound dissolved in white oil (4.1) to provide a zirconium content in the range of 12 % (*m/m*) to 18 % (*m/m*).

4.5 Zirconium solution B

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

5 Apparatus

5.1 Wavelength-dispersive X-ray fluorescence spectrometer, use any suitable spectrometer, provided that the design incorporates the features given 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 1)	30 kV to 50 kV
Current 1)	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

1) Lower power systems may be used, provided that they have 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** or **ultrasonic stirrer**.

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

6 Samples and sampling

6.1 Unless otherwise specified, samples shall be taken according to 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 which renders the sample liquid, and homogenize, using the homogenizer (5.3) as necessary.

NOTE 3 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).

NOTE 4 The approximate quantities of sulfur compounds (4.2) to be added to 100 g of white oil (4.1) to prepare the stock solutions are:

DBT (4.2.1) 16,75 g [2,5 % (*m/m*)] and 0,56 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*)]

NOTE 5 It is recommended that a polytetrafluorethylene or glass-coated magnetic stirrer and stirring device are used to mix the contents of the flask.

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

$$w_{S,2} = \frac{m_c \times w_{S,1}}{m_c + m_o} \quad \text{. . (1)}$$

where

m_c is the mass, in grams, of sulfur compound;

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

m_o is the mass, in grams, of white oil.

7.3 Preparation of standard solutions

7.3.1 High range

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 of the standard solution, $w_{\mathrm{S},3}$, to the nearest 0,001 % (*m/m*), using the following equation:

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

where

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

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

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

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

7.3.2 Low range

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 given in 7.3.1.

7.4 Preparation of calibration solutions

7.4.1 High range

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

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 timescale specified.

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

NOTE 6 The stability of prepared standards, under the above storage conditions, has been found to be 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

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-K_α (0,537 3 nm) and Zr-$L_{\alpha 1}$ (0,607 0 nm) fluorescence radiation.

Calculate the gross count ratio, R, using the following equation:

$$R = \frac{I_S}{I_{Zr}} \qquad \text{. . . (3)}$$

Construct a calibration curve (see note 7) by plotting the gross count ratio, R, against the sulfur content, as a percentage by mass of the calibration solutions between 0,1 % (*m/m*) and 2,5 % (*m/m*).

8.3 Low-range calibration curve

Proceed as in 8.2 using the low-range calibration solutions (7.4.2), and also measure the background radiation, I_u, 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 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-$L_{\alpha 1}$ line over the total measurement period.

Calculate the net count ratio, R_0, using the following equation:

$$R_0 = \frac{I_S - I_u}{I_{Zr} - I_u} \qquad \text{. . . (4)}$$

Construct a calibration curve (see note 7) by plotting the net count ratio, R_0, against the sulfur content, as a percentage by mass, of the calibration solutions between 0,001 0 % (*m/m*) and 0,1 % (*m/m*).

8.4 Checking

Check the calibration curves regularly. In regular use, check at least two points on each calibration curve not less frequently than every six months. If the check result differs from the curve by more than the repeatability of this International Standard, a new calibration curve shall be constructed.

9 Procedure

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

Weigh 20,00 g ± 0,01 g of the sample to be analysed (see note 3) 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 according to 8.2 and calculate the gross count ratio, R.

9.2 Samples with sulfur contents between 0,0010 % (*m/m*) and 0,1 % (*m/m*)

Weigh 20,00 g ± 0,01 g of the sample to be analysed (see note 3) 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 according to 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 9.1.

NOTE 7 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 0,001 % (m/m) between 0,010 % (m/m) and 0,099 % (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 successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the normal and correct operation of the test method, exceed the values in table 2 only in 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 nominally identical test material would, in the normal and correct operation of the test method, exceed the values in table 2 only in 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 to 0,029	0,002	0,005
0,030 to 0,049	0,003	0,005
0,050 to 0,099	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;

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

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

d) the results of the test (see clause 11);

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

f) the date of the test.