भारतीय मानक

Indian Standard

IS 1448 (Part 199) : 2024
ISO 8754 : 2003

पेट्रोलियम और उसके उत्पाद — परीक्षण पद्धतियाँ

भाग 199 गंधक की मात्रा का निर्धारण — ऊर्जा-वितरणशील एक्स-रे फ्लोरेसेंस स्पेक्ट्रोमेट्री

Petroleum and its Products — Methods of Test

Part 199 Determination of Sulfur Content — Energy-Dispersive X-Ray Fluorescence Spectrometry

ICS 75.080

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November 2024 **Price Group 6**

Methods of Sampling and Test for Petroleum and Related Products of Natural or Synthetic Origin (excluding bitumen) Sectional Committee, PCD 01

NATIONAL FOREWORD

This Indian Standard which is identical to ISO 8754 : 2003 ‘Petroleum products — Determination of sulfur content — Energy-dispersive X-ray fluorescence spectrometry’ issued by the International Organization for Standardization (ISO) was adopted by the Bureau of Indian Standards on the recommendation of the Methods of Sampling and Test for Petroleum and Related Products of Natural or Synthetic Origin (excluding bitumen) Sectional Committee and approval of the Petroleum, Coal and Related Products Division Council.

The text of ISO standard has been approved as suitable for publication as an Indian Standard without deviations. Certain conventions are, however, not identical to those used in Indian Standards. Attention is particularly drawn to the following:

a) Wherever the words ‘International Standard’ appear referring to this standard, they should be read as ‘Indian Standard’; and

b) Comma (,) has been used as a decimal marker while in Indian Standards, the current practice is to use a point (.) as the decimal marker.

This standard is one among the IS 1448 series of Indian Standards on ‘Methods of test for petroleum and its products’. Information on all parts of the IS 1448 series published under the general title 'Petroleum and its products – Methods of Test', can be accessed from the BIS website www.bis.gov.in.

In this adopted standard, reference appears to certain International Standard for which Indian Standard also exist. The corresponding Indian Standard, which is to be substituted in their respective places, is given below along with their degree of equivalence for the edition indicated:

International Standard	*Corresponding Indian Standard*	*Degree of Equivalence*
ISO 3170 Petroleum liquids — Manual sampling	IS 1447 (Part 1) : 2021 Methods of sampling of petroleum and its products: Part 1 Manual sampling (*second revision*)	Not Equivalent

The Committee has reviewed the provisions of the following International Standards referred in this adopted standard and has decided that they are acceptable for use in conjunction with this standard:

International Standard	*Title*
ISO 3171 : 1988	Petroleum liquids — Automatic pipeline sampling

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 2022 ‘Rules for rounding off numerical values (*second revision*)’.

Introduction

Specialized procedures, using the analytical technique described in this International Standard, for automotive fuels with sulfur contents below 0,20 % (*m/m*), are under development.

Indian Standard

PETROLEUM AND ITS PRODUCTS — METHODS OF TEST

PART 199 DETERMINATION OF SULFUR CONTENT — ENERGY-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 petroleum products, such as naphthas, unleaded motor gasolines, middle distillates, residual fuel oils, base lubricating oils and components. The method is applicable to products having sulfur contents in the range 0,03 % (m/m) to 5,00 % (m/m).

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

Heavy metal additives, such as lead alkyls, may interfere with the determination. Elements such as silicon, phosphorus, calcium, oxygen, potassium, zinc, molybdenum, barium and halogens interfere, if present in concentrations of more than a few hundred milligrams per kilogram. Some modern instruments allow the analyst to compensate for matrix and spectral interferences by spectra deconvolution and inter-element correction by multiple regression.

For samples varying in composition of aromatic hydrocarbons and paraffinic hydrocarbons, the ratio of carbon to hydrocarbon in a sample (C/H ratio) may also interfere with the determination, when the ratio of the sample differs by one or more from that of the reference materials from which the calibration is obtained.

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:—[1], *Petroleum liquids — Manual sampling*

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

3 Principle

The test portion is placed in the beam emitted from an X-ray source. The excitation energy may be derived from a radioactive source, such as ^{55}Fe, or from an X-ray tube. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with a calibration graph plotting counts against sulfur content as percentage by mass [% (m/m)], on a series of calibration samples covering the range of sulfur contents under examination.

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[1] To be published. (Revision of ISO 3170:1988)

4 Reagents and materials

4.1 White oil (light paraffin oil), of high purity grade, with a maximum sulfur content of 20 mg/kg.

For measurements at very low levels of sulfur content [below approximately 0,1 % (m/m)], matrix effects are minimized if a diluent of a type similar to the product being analysed is used for the production of the calibration standards described in Clause 8. Such a diluent should be of very low sulfur content, preferably below 2 mg/kg.

4.2 Sulfur compounds, of known sulfur content, used for the preparation of the primary standards.

NOTE 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 concentrations and nature of all impurities are to be known.

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

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

4.2.3 Thionaphthene (benzothiophene) (TNA), with a nominal sulfur content of 23,89 % (m/m).

4.3 Certified reference materials: use materials from a national standards body or accredited supplier, with a range of certified sulfur contents for the production of calibration curves for routine analysis. However, particularly for some heavier materials, the excitation is slightly affected by the background matrix. Therefore, in cases of dispute, the parties shall agree on a common range of certified standards, or shall both prepare standards from the materials described in 4.1 and 4.2.

5 Apparatus

5.1 Energy-dispersive X-ray fluorescence analyser: use any suitable model, provided that the design incorporates the features given in 5.1.1 to 5.1.6. It shall be set up according to the manufacturer's instructions.

5.1.1 Source of X-ray excitation, with significant X-ray flux at energies above 2,5 keV.

5.1.2 Removable sample cup, providing a sample depth of at least 3 mm, and equipped with replaceable X-ray transparent film.

NOTE Window material is normally 6 µm polyester, polypropylene or polycarbonate film. Commercial polyester film may contain small but variable amounts of calcium, which may interfere. Samples of very high aromatic content may dissolve polycarbonate film.

5.1.3 X-ray detector, with high sensitivity at 2,3 keV.

5.1.4 Filters, or other means of discriminating between sulfur Kα radiation and other X-rays.

5.1.5 Signal-conditioning electronics, that include the functions of pulse counting and pulse-height analysis.

5.1.6 Display or **printer**, that provides a readout in counts, sulfur content as a percentage by mass [% (m/m)], or both.

CAUTION — If the analyser contains a radioactive source, the equipment and manner of use shall comply with the regulations governing the use of ionizing radiation and/or recommendations of the International Commission on Radiological Protection. The radiation source shall be checked for radiation leakage at intervals as required by the regulations. All attention to the source shall only be carried out by fully trained and competent persons, using the correct shielding techniques.

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

5.3 **Mixer**, of non-aerating, high-speed shear type.

5.4 **Containers**: either flasks of 100 ml capacity, narrow-necked, conical, and made of borosilicate glass, with optional stoppers for use with volatile samples, or bottles of similar capacity fitted with polyethylene or polytetrafluoroethylene seals in the closure.

6 Samples and sampling

6.1 Unless otherwise specified, samples shall be taken in accordance with the procedures 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 mixer (5.3) as necessary.

7 Apparatus preparation

7.1 Analyser

Wherever possible, the instrument (see 5.1) shall be continuously switched on to maintain optimum stability.

7.2 Sample cups

Thoroughly clean and dry the sample cups before use. Do not re-use disposable cups. Keep handling of window material to the absolute minimum.

8 Calibration

8.1 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 calibration standards.

8.2 Preparation of primary standards

8.2.1 Prepare a range of at least three primary standards. Either use primary standards to prepare the calibration standards by dilution with white oil (4.1), or prepare the complete range of calibration standards directly by the procedure given in 8.2.2.

8.2.2 Weigh, to the nearest 0,1 mg, the appropriate quantity of white oil (see Table 1), into a container (5.4) and add the appropriate quantity of the selected sulfur compound (4.2), weighed to the nearest 0,1 mg. Mix the contents of the container thoroughly at room temperature.

It is recommended that an inert magnetic stirrer and stirring device are used to mix the contents of the container. In the case of volatile liquids, the container should be stoppered, and the mixture gently shaken or agitated.

Calculate the exact sulfur content, w_S, expressed as a percentage by mass [% (m/m)] to three decimal places in each case, from the amounts of white oil and sulfur compound used as follows:

$$w_\mathrm{S} = \frac{m_1 \times w_\mathrm{S,c}}{m_1 + m_2}$$

where

m_1 is the mass of sulfur compound, expressed in grams;

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

m_2 is the mass of white oil, expressed in grams.

Table 1 — Composition of primary standards based on nominal sulfur contents

Approximate sulfur content % (m/m)	**White oil** g	**DBT** (4.2.1) g	**DBS** (4.2.2) g	**TNA** (4.2.3) g
5	40,0	16,1	11,8	10,6
4	40,0	11,95	8,95	8,05
3	40,0	8,3	6,3	5,75
2	45,0	5,85	4,5	4,1
1,5	45,0	4,25	3,3	3,0
1	45,0	2,75	2,15	1,95
0,5	50,0	1,5	1,15	1,05
0,3	50,0	0,9	0,7	0,65
0,1	50,0	0,3	0,25	0,2
0,07	50,0	0,21	0,18	0,14
0,05	50,0	0,14	0,11	0,1
0,03	50,0	0,09	0,07	0,07

8.3 Calibration standards

For analysers without curvature fitting, use calibration standards in four ranges (see Table 2). For analysers with curvature fitting, or those which require manual graph drawing, combine two adjacent ranges, using all the standards within those ranges.

Table 2 — Calibration standard ranges

Range	**Sample sulfur content** % (m/m)	**Standard sulfur content** % (m/m)				
1	0,03 to 0,10	0,00	0,03	0,05	0,07	0,10
2	$> 0{,}10$ and $\leqslant 0{,}5$	0,00	0,1	0,3	0,5	
3	$> 0{,}5$ and $\leqslant 2{,}0$	0,5	1,0	1,5	2,0	
4	$> 2{,}0$ and $\leqslant 5{,}0$	2,0	3,0	4,0	5,0	

8.4 Storage of standards

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

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

NOTE The stability of stored standards, under the above storage conditions, has been found to exceed three months.

8.5 Calibration procedure

Prepare the sample cup (5.1.2) in accordance with the manufacturer's instructions. Cover the base of the cup with window film, avoiding skin contact, and fill to a depth of between 3 mm and 20 mm with the calibration standard. Ensure that the window is smooth and taut and that there are no air bubbles between the window and the liquid.

Obtain a reading on each standard, using the recommended counting time for the instrument.

Usually, it is sufficient to obtain a single reading for each standard. However, it may be advisable to immediately repeat the measuring procedure up to four times, using freshly prepared cups and fresh portions of the standard, if there is an indication of erratic or erroneous results.

Taking consecutive single readings using the same cup and standard portion is not recommended. Cups and films will change shape as they are measured, or waiting to be measured. In addition, samples may be volatile and change composition with time.

From the data obtained, calculate the average, if necessary, for each sulfur content. From the resulting data set, construct the calibration curve by linear regression, either manually or with the aid of a computer, using sulfur content as an independent variable and the readings as dependent variables.

8.6 Checking

8.6.1 Short-term checking

In regular use, check at least two points on each calibration curve not less frequently than weekly. This shall be accomplished by using set-up standards, which have been assigned and selected from an inspection of the calibration curve. If the check results differ from the curve by more than the repeatability, repeat the calibration procedure.

8.6.2 Long-term checking

Carry out more elaborate checks at intervals not greater than three months, following the procedure described in 8.5.

9 Procedure

Prepare and fill the sample cup with the test portion as described in 8.5, and obtain two counts using the manufacturer's recommended counting time for the instrument.

For volatile samples, care should be taken to prevent window bowing if the sample cup is capped. Venting may be necessary to avoid excessive pressure build-up, but if losses due to evaporation are noted during measurement, a fresh portion of sample in a new cup should be used for the second count, and the counting time reduced, even at the expense of counting precision.

Calculate the average count for the sample.

NOTE Modern instruments may incorporate this calculation.

10 Calculation

Read the concentration of sulfur in the sample from the calibration curve, using the average count for each test portion, or by direct reading from those analysers which have computing facilities.

11 Expression of results

Report the result to the nearest 0,01 % (m/m) sulfur content for values between 0,10 % (m/m) and 5,00 % (m/m), and to the nearest 0,001 % (m/m) sulfur content for values between 0,030 % (m/m) and 0,099 % (m/m).

12 Precision

12.1 General

The precision was determined by statistical examination, in accordance with ISO 4259:1992, *Petroleum products — Determination and application of precision data in relation to methods of test*, of interlaboratory test results on a matrix of samples including gasolines, kerosines, gas oils and residual fuel oils with sulfur contents from below 0,10 % (m/m) to above 5,0 % (m/m).

NOTE The precision given in 12.2 and 12.3 was developed by analysis of the combined test results from three large precision-evaluation programmes, one sponsored by ASTM in the USA in 1995/1996 and one sponsored by the IP in Europe in 1997 on the range of fuels covering the whole scope of the test method, and the third sponsored by AFNOR in France covering automotive gasolines and diesel fuels of low sulfur content only. Both instrument types were included in all three programmes.

12.2 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 following values in only one case in twenty:

$r = 0{,}045\,4\ (X + 0{,}05)$, for values $\geqslant 0{,}03$ % (m/m) and $\leqslant 0{,}05$ % (m/m);

$r = 0{,}021\,5\ (X + 0{,}15)$, for values $> 0{,}05$ % (m/m) and $\leqslant 5{,}00$ % (m/m);

where X is the average of the results being compared, in % (m/m).

12.3 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 following values in only one case in twenty:

$R = 0{,}178\,1\ (X + 0{,}05)$, for values $\geqslant 0{,}03$ % (m/m) and $\leqslant 0{,}05$ % (m/m);

$R = 0{,}081\,2\ (X + 0{,}15)$, for values $> 0{,}05$ % (m/m) and $\leqslant 5{,}00$ % (m/m);

where X is the average of the results being compared, in % (m/m).

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 result of the test (see Clause 11);

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

e) the date of the test.

Bureau of Indian Standards

BIS is a statutory institution established under the *Bureau of Indian Standards Act*, 2016 to promote harmonious development of the activities of standardization, marking and quality certification of goods and attending to connected matters in the country.

Review of Indian Standards

Amendments are issued to standards as the need arises on the basis of comments. Standards are also reviewed periodically; a standard along with amendments is reaffirmed when such review indicates that no changes are needed; if the review indicates that changes are needed, it is taken up for revision. Users of Indian Standards should ascertain that they are in possession of the latest amendments or edition by referring to the website-www.bis.gov.in or www.standardsbis.in.

This Indian Standard has been developed from Doc No.: PCD 01 (23725).

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

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