INTERNATIONAL STANDARD

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Petroleum products — Determination of low concentration of sulfur in automotive fuels — Energy-dispersive X-ray fluorescence spectrometric method

Produits pétroliers — Détermination de la teneur en soufre en faible concentration dans les carburants pour automobiles — Méthode spectrométrique de fluorescence de rayons X dispersive en énergie

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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 13032 was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 19, *Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin,* in collaboration with ISO Technical Committee TC 28, *Petroleum products and lubricants,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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Introduction

This International Standard is directed specifically at the lower end of the concentration range covered in ISO 20847^[2]. By selecting the instrument type, a better signal-to-background ratio for sulfur K-L_{2,3} emission is assured. A knowledge of the general composition of the sample for analysis is advantageous in obtaining the best test result.

NOTE IUPAC X-ray line notation (S K-L_{2,3}) is used in this International Standard; the corresponding Siegbahn X-ray line notation (S-K α) is being phased out.

Where matrix matching is not used and where the C:H mass ratio of the test sample is known or can be determined, accuracy can be improved by the use of Equation (A.1) (see A.2.3) to correct the result to the C:H mass ratio of the calibration standards, i.e. the reference diluent oil (see 4.1).

Some instruments include the capability for instrument-based matrix correction; notes on the use of this approach to compensate for matrix effects in the test sample are provided in A.3 for information.

This International Standard is based on IP test method PM DU^[3] developed by the Energy Institute.

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Petroleum products — Determination of low concentration of sulfur in automotive fuels — Energy-dispersive X-ray fluorescence spectrometric method

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 an energy dispersive X-ray fluorescence (EDXRF) test method for the determination of sulfur content in automotive gasoline containing up to 3,7 % (m/m) oxygen [including those blended with ethanol up to 10 % (V/V)], and in diesel fuels [including those containing up to about 10 % (V/V)] fatty acid methylester (FAME)] having sulfur contents in the range 8 mg/kg to 50 mg/kg.

Other products can be analysed and other sulfur contents can be determined according to this test method; however, no precision data for products other than automotive fuels and for results outside the specified range have been established for this International Standard.

For reasons of spectral overlap, this international Standard is not applicable to leaded automotive gasoline, gasoline having a content of greater than 8 mg/kg lead replacement or to product and feedstock containing lead, silicon, phosphorus, calcium, potassium of halides at concentrations greater than one tenth of the concentration of sulfur measured or more than 10 mg/kg, whichever is the greater.

NOTE For the purposes of this International Standard, the terms "% (*m/m*)" and "% (*V/V*)" are used to represent the mass fraction, μ , and the volume fraction, ϕ , 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 test portion, in a cup fitted with an X-ray transparent window, is placed in a beam of exciting radiation from an X-ray tube. The intensity of the sulfur K- $L_{2,3}$ characteristic X-radiation is measured and the accumulated count is compared with a calibration curve constructed from sulfur standards covering the range of sulfur contents under examination.

NOTE The exciting radiation can be either direct or indirect via a polarizing or secondary target.

4 Reagents and materials

4.1 Diluent oil

The reference diluent oil is white oil (light paraffin oil) of high purity grade, with a maximum sulfur content of 0,5 mg/kg. However, if only one type of matrix is to be analysed (e.g. motor gasoline), the accuracy of results

may be improved by using a matrix-matched diluent. These should match, approximately, the aromatic and oxygen contents of the material to be analysed and should consist of high-purity components of less than 0,5 mg/kg sulfur content.

NOTE 1 Suitable components for the matched matrix diluent include *n*-heptane, 2,2,4-trimethylpentane, toluene, xylenes, ethanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE) and tertiary amyl methyl ether (TAME).

NOTE 2 For the analysis of diesel fuels containing FAME, the accuracy of results can be improved by use of a matched matrix diluent oil of the white oil with FAME.

4.2 Sulfur compounds

4.2.1 General

Sulfur compounds of known sulfur content shall be used for the preparation of the primary standards. The compounds given in 4.2.2 to 4.2.5 are suitable and their nominal sulfur contents are given. Where the purity of these compounds is less than 99 % (m/m), either the concentrations and nature of all impurities are to be known or certified reference materials (CRMs) shall be used instead.

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

4.2.3 Dibutylsulfide (DBS), with a nominal sulfur content of 21,915 % (*m/m*), or

- **4.2.4** Thionaphthene (Benzothiophene) (TNA), with a nominal sulfur content of 23,890 % (*m/m*), or
- **4.2.5** Dibutyldisulfide (DBDS), with a nominal sulfur content of 35,950 % (*m/m*).
- 4.3 Reference materials (CRMs) ISO 13032:2012

CRMs from accredited suppliers, containing a range of sulfur concentrations, are suitable alternatives to the compounds listed in 4.2.2 to 4.2.5 for use as calibration standards.

4.4 Quality control samples

Stable samples representative of the materials being analysed, which have a sulfur content that is known by this test method over a substantial period of time, or are supplied commercially with a certified value. Ensure, before use, that the material is within its shelf-life.

5 Apparatus

5.1 Energy-dispersive X-ray fluorescence instrument

5.1.1 Performance characteristics.

For a 10 mg/kg sulfur standard (see 8.3), the instrument shall be capable of meeting the following performance characteristics:

$$\left(R_{\rm s}-R_{\rm b}\right)/\sqrt{R_{\rm b}} \ge 1,3\tag{1}$$

and

$$C_V(R_s) < 5\%$$

where

(2)

- *R*_s is the gross count rate (counts per second) for the sulfur region of interest for a 10 mg/kg sulfur standard;
- *R*_b is the gross count rate (counts per second) for the same region of interest for a blank sample [diluent oil (4.1)];
- C_V is the coefficient of variation (relative standard deviation) based on 10 individual measurements of the calibration standard.

The 10 mg/kg sulfur standard shall be a CRM (4.3) or shall be prepared from one of the compounds given in 4.2.2 to 4.2.5 following the procedures described in Clause 8.

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

For X-ray detectors with a resolution greater than 200 eV at 2,3 keV, all characteristic X-ray lines originating from the X-ray tube anode shall have an energy above 3,3 keV to ensure minimal background variation due to scatter from the X-ray tube anode lines.

5.1.3 Removable sample cup, providing a sample depth of at least 5 mm and equipped with replaceable X-ray transparent film.

NOTE The transparent film is normally polyester or polycarbonate film with a thickness of between 2 μ m and 6 μ m. Polyester film is the preferred choice as samples of very high aromatic content can dissolve polycarbonate film. There are possibly trace amounts of silicon, calcium and sulfur in some types of film. However, the effects are normally cancelled out where 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. **PREVIEW**

5.1.4 X-ray detector, with a resolution not exceeding 800 eV at 2,3 keV.

5.1.5 Means of discriminating between <u>Sulfur K-L23</u> characteristic X-radiation and other X-rays of higher energy (if required; for example/filters) standards/sist/e2ec124c-68c3-4b7a-ace4-311a30d8e5c3/iso-13032-2012

5.1.6 Signal conditioning and data-handling electronics, including the functions of pulse counting and an energy region for the S peak as a minimum.

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

5.3 Mixer, magnetic stirrer with PTFE-coated stirring rods.

5.4 Flasks, of 100 ml capacity, narrow-necked, conical and made of borosilicate glass.

6 Sampling and sample handling

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

6.2 Store samples which contain light fractions (e.g. motor gasoline and naphtha) in a refrigerator (spark free).

- 6.3 Mix samples by means of gentle shaking by hand prior to the removal of the test portion.
- 6.4 Allow test portions to attain ambient temperature prior to analysis.

NOTE Additional sample handling recommendations are given in IP 558 (ASTM D7343^[4]).

7 Apparatus preparation

7.1 Analyser

7.1.1 Set up the analyser (5.1) in accordance with the manufacturer's instructions. Wherever possible, the instrument shall be continuously switched on to maintain optimum stability.

7.1.2 If required, purge the optical system with helium (minimum 99 % purity) following the manufacturer's guidelines on flush time and flow rate to ensure stability of measurements.

7.2 Sample cups

It is recommended that disposable sample cups be used. If disposable cups are not used, thoroughly clean the sample cups with an appropriate solvent and dry before use.

Do not re-use disposable cups.

Use the same batch of window material for each run of verification and sampling analysis (see Note to 5.1.3).

Keep handling of window material to the absolute minimum. Follow the guidelines given in Annex B.

NOTE Differences in window material thickness between batches or the presence of even partial finger marks are sufficient to affect results.

8 Calibration

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8.1 General

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Use either CRMs (4.3) or primary standards prepared from the selected sulfur compound (4.2) dissolved in diluent oil (4.1) as a basis for the preparation of the two primary standards. The user shall always validate his/her calibration with CRMs whose matrices match his/her samples.

NOTE Recommendations on selection of diluent oil are provided in Annex A. Accuracy can be improved by utilizing the manufacturer's recommended instrument-based matrix correction (see Annex A). For this method, see the manufacturer's recommended corrections.

8.2 Preparation of primary standards

8.2.1 Prepare two primary standards with sulfur contents of approximately 500 mg/kg and 1 000 mg/kg.

8.2.2 Weigh, to the nearest 0,1 mg, the appropriate quantity of the selected sulfur compound (4.2) or CRM (4.3) (see Table 1) into a flask (5.4) and add the appropriate quantity of diluent oil (4.1), weighed to the nearest 0,1 mg.

Mix the contents of the flask thoroughly at room temperature using the mixer (5.3).

(3)

	Approximate sulfur content	White oil	DBT ^a	DBS ^b	TNAC
	mg/kg	g	g	g	g
	1 000	50,0	0,29	0,23	0,21
	500	50,0	0,144	0,114	0,105
а	See 4.2.2.				
b	See 4.2.3.				
С	See 4.2.4.				

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

8.2.3 Calculate the sulfur content, *S*, in milligrams per kilogram, to one decimal place in each case, from the amounts of diluent oil and sulfur compound used, as follows:

$$S = 10\ 000 \times \frac{(m_{\rm s}c_{\rm s} + m_{\rm d}c_{\rm d})}{(m_{\rm s} + m_{\rm d})}$$

where

 $m_{\rm S}$ is the mass of sulfur compound, expressed in grams (g);

- c_s is the sulfur content of the sulfur compound, expressed as a mass percentage [% (m/m)];
- c_d is the sulfur content of the diluent oil, expressed as a mass percentage [% (m/m)];
- m_d is the mass of diluent oil, expressed in grams (d)eh.ai)

8.2.4 Store primary standards in tightly closed glass containers in a cool, dark place, preferably in a refrigerator. Before use, examine for any phase separation of discoloration, shake vigorously and let stand to allow for removal of air bubbles. Discard any standard that shows sediment, phase separation or discoloration.

NOTE Stability trials have shown that primary standards are stable for up to six months if stored in a refrigerator.

8.3 Calibration standards

8.3.1 Prepare calibration standards of nominal concentrations as shown in Table 2, from the primary standards (8.2) in the selected diluent oil (4.1) and calculate the exact sulfur content of the calibration standard, S_x , in milligrams per kilogram, as follows:

$$S_{x} = \frac{(m_{s,x} c_{s,x} + m_{d} c_{d})}{(m_{s,x} + m_{d})}$$

where

 $m_{S,x}$ is the mass of sulfur primary standard, expressed in grams (g);

- $c_{s,x}$ is the sulfur content of the primary standard, expressed in milligrams per kilogram (mg/kg);
- cd is the sulfur content of the diluent oil, expressed in milligrams per kilogram (mg/kg);
- m_d is the mass of diluent oil, expressed in grams (g).

Prepare calibration standards of nominal sulfur content of 5 mg/kg, 10 mg/kg and 50 mg/kg from the 500 mg/kg primary standard and calibration standards of nominal sulfur content of 30 mg/kg, 70 mg/kg and 100 mg/kg from the 1 000 mg/kg primary standard.

(4)