SLOVENSKI STANDARD
oSIST prEN ISO 13032:2023

01-julij-2023

Naftni proizvodi - Določevanje nizke koncentracije žvepla v gorivih za motorna vozila - Metoda z energijsko-disperzivno rentgensko fluorescenčno spektrometrijo (ISO/DIS 13032:2023)

Petroleum products - Determination of low concentration of sulfur in automotive fuels - Energy-dispersive X-ray fluorescence spectrometric method (ISO/DIS 13032:2023)

Mineralölerzeugnisse - Bestimmung niedriger Schwefelgehalte in Kraftstoffen - Energiedispersives Röntgenfluoreszenzspektrometrieverfahren (ISO/DIS 13032:2023)

Produits pétroliers et connexes - Détermination de la teneur en soufre en faible concentration dans les carburants pour automobiles - Méthode spectrométrique de fluorescence de rayons X dispersive en énergie(ISO/DIS 13032:2023)

Ta slovenski standard je istoveten z: **prEN ISO 13032**

ICS:

75.160.20	Tekoča goriva	Liquid fuels

oSIST prEN ISO 13032:2023 **en,fr,de**

DRAFT INTERNATIONAL STANDARD

ISO/DIS 13032

ISO/TC **28**

Secretariat: **NEN**

Voting begins on:
2023-05-25

Voting terminates on:
2023-08-17

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

ICS: 75.160.20

This document is circulated as received from the committee secretariat.

ISO/CEN PARALLEL PROCESSING

Reference number
ISO/DIS 13032:2023(E)

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Published in Switzerland

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 28, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*, in collaboration with CEN/TC 19, *Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin*.

This second edition cancels and replaces the first edition (ISO 13032:2012), which has been technically revised.

The main changes compared to the previous edition are as follows:

— extension of the Scope to include hydrotreated vegetable oil (HVO), synthetic fuel Gas To Liquid (GTL) and neat fatty acid methyl ester (FAME);

— update of the precision details.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document is directed specifically at the lower end of the concentration range covered in ISO 20847. 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. Compared to the previous version new fuels have been added to the scope. In addition, the precision and bias statements as well as the concentration range were updated based on results of a new interlaboratory study. This has been done for gasoline and diesel type fuels as well as for FAME type samples.

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

WARNING — the use of this document can involve hazardous materials, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of users of this document to take appropriate measures to ensure the safety and health of personnel prior to application of the document, and fulfil other applicable requirements for this purpose.

1 Scope

This document specifies an energy dispersive X-ray fluorescence (EDXRF) test method for the determination of sulfur content in automotive gasoline containing up to 3,7 % oxygen by mass [including those blended with ethanol up to 10 % by volume] having sulfur contents in the range of 6,9 mg/kg to 56,7 mg/kg., and in diesel fuels [including those containing up to about 30 % fatty acid methyl ester (FAME) by volume], in synthetic fuels such as Hydrotreated Vegetable Oil (HVO), Gas To Liquid (GTL) and neat FAME having sulfur contents in the range of 5,0 mg/kg to 60,2 mg/kg.

When analysing FAME, the corresponding procedures are followed (5.2.6, 9.1, and 9.4.5).

The sulfur content in other products 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 document.

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

NOTE 1 IUPAC X ray line notation (S K-$L_{2,3}$) is used in this document; the corresponding Siegbahn X-ray line notation (S Kα οr Σ K$\alpha_{1,2}$) is being phased out.

NOTE 2 This document is based on IP test method PM DU[3] developed originally by the Energy Institute, London, UK.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

ISO 17034, *General requirements for the competence of reference material producers*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 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 number of counts in a given time or a count rate is compared with a calibration curve constructed from sulfur standards covering the range of sulfur contents under examination.

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

5 Reagents and materials

5.1 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.

For the analysis of FAME an adjustment of the oxygen content to the sample matrix shall be done. The use of a mixture of white oil with methyl oleate (see 5.2.6) or organic acid (see 5.2.7) is recommended as diluent oil,

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 composed of a mixture of white oil and methyl oleate (see 5.2.6) or organic acid, to adjust the oxygen content and the sample matrix.

5.2 Sulfur compounds

5.2.1 General

Sulfur compounds of known sulfur content shall be used for the preparation of the primary standards. The compounds given in 5.2.2 to 5.2.5 are suitable and their nominal sulfur contents are given. Where the purity of these compounds is less than 99 % by mass, either the concentrations and nature of all impurities are to be known or certified reference materials (CRMs) (5.3) shall be used instead.

5.2.2 Dibenzothiophene (DBT), with a nominal sulfur content of 17,399 % by mass, or

5.2.3 Dibutylsulfide (DBS), with a nominal sulfur content of 21,915 % by mass, or

5.2.4 Thionaphthene (Benzothiophene) (TNA), with a nominal sulfur content of 23,890 % by mass, or

5.2.5 Dibutyldisulfide (DBDS), with a nominal sulfur content of 35,950 % by mass.

5.2.6 Methyl oleate, for use as a blank solution with a sulfur content of less than 1 mg/kg when FAME is analyzed. Check the blank solution prior to use with the spectrometer (6.1). A signal for sulfur

shall not be detectable (i.e. the intensity shall be lower that the intensity equivalent to 1 mg/kg). Other oxygen containing and sulfur-free blank solutions, such as octanol, may also be used. Methyl oleate may also be used in combination with white oil to make a matrix-matched base for diesel fuels containing FAME.

5.2.7 Organic acid, for use as a blank solution with a sulfur content of less than 1 mg/kg when FAME is analyzed. Check the blank solution prior to use with the spectrometer (6.1). A signal for sulfur shall not be detectable (i.e. the intensity shall be lower that the intensity equivalent to 1 mg/kg). Other oxygen containing and sulfur-free blank solutions, such as octanol, may also be used. Organic acid can also be used in combination with white oil to make a matrix-matched base for diesel fuels containing FAME.

5.3 Reference materials (CRMs)

CRMs from suppliers complying with ISO 17034, containing a range of sulfur concentrations, are suitable alternatives to the calibration standard solutions based on compounds listed in 5.2.2 to 5.2.5 for use as calibration standards.

5.4 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.

6 Apparatus

6.1 Energy-dispersive X-ray fluorescence instrument

6.1.1 Performance characteristics.

For a 10 mg/kg sulfur standard (see 8.3), the instrument shall be capable of meeting the performance characteristics as described by Formula (1) and Formula (2):

$$\left(R_s - R_b\right)/\sqrt{R_b} \geq 1{,}3 \tag{1}$$

and

$$C_V(R_s) < 5\ \% \tag{2}$$

where

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 (5.1, 5.2.6, 5.2.7 or a mixture of one of the last two mentioned with 5.1)];

C_V is the coefficient of variation (relative standard deviation[1)]
The predecessor term "relative standard deviation" is deprecated by the term “coefficient of variation”.

) based on 10 individual measurements of the calibration standard.

1) The predecessor term "relative standard deviation" is deprecated by the term “coefficient of variation”.