



**International  
Standard**

**ISO 13032**

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

**Second edition  
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*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*

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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 document 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](http://www.iso.org/directives)).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at [www.iso.org/patents](http://www.iso.org/patents). ISO shall not be held responsible for identifying any or all such patent rights.

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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](http://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 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 accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 13032:2012), which has been technically revised. [standards.iteh.ai/catalog/standards/iso/4e9a4094-82f8-4ac3-a256-f19dfc02764c/iso-13032-2024](http://standards.iteh.ai/catalog/standards/iso/4e9a4094-82f8-4ac3-a256-f19dfc02764c/iso-13032-2024)

The main changes are as follows:

- extension of the Scope to include paraffinic diesel fuel and neat fatty acid methyl ester (FAME);
- update of precision statements as well as the concentration range which are based on results of a new interlaboratory study, for gasoline and diesel type fuels, and FAME type samples.

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](http://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<sub>2,3</sub> emission is ensured. 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<sub>2,3</sub>) is used in this document; the corresponding Siegbahn X-ray line notation (S K $\alpha$  or S K $\alpha$ <sub>1,2</sub>) is being phased out.

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# 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 to 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 fuels. This document is applicable to:

- 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,
- diesel fuels including those containing up to about 30 % fatty acid methyl ester (FAME) by volume, paraffinic diesel fuel, and neat FAME, having sulfur contents in the range of 5,0 mg/kg to 60,2 mg/kg.

The sulfur content in other products can be determined according to the test method specified in this document; 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.

## 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*

## 3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology 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<sub>2,3</sub> characteristic X-radiation is measured. The accumulated number of counts in a given time or count rate is compared with a calibration curve constructed from sulfur standard solutions 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 required to be analysed (e.g. motor gasoline), the accuracy of results can 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, the oxygen content shall be adjusted to the sample matrix. 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 a 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 Sulfur compounds of known sulfur content.** These 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 shall 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.

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

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

**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 analysed. 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 than 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 analysed. 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 than the intensity equivalent to 1 mg/kg). Other oxygen-containing and sulfur-free blank solutions, such as octanol, may also be used. Organic acid may also be used in combination with white oil to make a matrix-matched base for diesel fuels containing FAME.



### 5.3 Reference materials

Certified reference materials (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

Quality control samples are 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. Before use, ensure that the material is within its shelf-life.

## 6 Apparatus

**6.1 Energy-dispersive X-ray fluorescence instrument**, with the following performance characteristics.

- a) For a 10 mg/kg sulfur standard (see [9.3](#)), the instrument shall be capable of meeting the performance characteristics as described by [Formulae \(1\)](#) and [\(2\)](#):

$$(R_s - R_b) / \sqrt{R_b} \geq 1,3 \quad (1)$$

and

$$C_V(R_s) < 5\% \quad (2)$$

where

$R_s$  is the gross count rate (expressed in counts per second) for the sulfur region of interest for a 10 mg/kg sulfur standard;

$R_b$  is the gross count rate (expressed in 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 either [5.2.6](#) or [5.2.7](#) with [5.1](#)];

$C_V$  is the coefficient of variation (relative standard deviation) based on 10 individual measurements of the calibration standard.

NOTE The term “relative standard deviation” is deprecated by the term “coefficient of variation”.

The 10 mg/kg sulfur standard shall be a CRM ([5.3](#)) or shall be prepared from one of the compounds given in [5.2.2](#) to [5.2.7](#) following the procedures described in [Clause 9](#).

- b) 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.

- c) Removable sample cup, providing a sample depth of at least 5 mm and equipped with replaceable X-ray transparent thin film. It is important that samples, standards, quality control standards and blanks are measured using the same batch of film to avoid bias.

- d) X-ray transparent film.

This is a thin film which shall possess the necessary combination of consistency and chemical and physical properties. It is typically made of polypropylene, polyester, polycarbonate or other materials with a thickness between 2 µm and 6 µm. Aromatics can dissolve polycarbonate or polypropylene films. It is thus preferable to choose films made of polyesters or other chemically resistant materials. Some types of film can

contain traces of silicon, calcium and sulfur. However, the effects are normally cancelled when samples and standards are analysed with the same batch of film.

- e) X-ray detector, with a resolution not exceeding 800 eV at 2,3 keV.
- f) Means of discriminating between sulfur K-L<sub>2,3</sub> characteristic X-radiation and other X-rays of higher energy, if required for example filters.
- g) Signal conditioning and data-handling electronics, including the functions of pulse counting and an energy region for the S peak as a minimum.

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

**6.3 Mixer**, magnetic stirrer with PTFE-coated stirring rods.

**6.4 Flasks**, narrow-necked, conical and made of borosilicate glass. Seal and stopper that are compatible with the matrix, sized so that the head space is minimal.

## 7 Sampling and sample handling

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

**7.2** Store samples which contain light fractions in a refrigerator (spark free).

**7.3** Mix samples by means of gentle shaking by hand prior to the removal of the test portion.

**7.4** Allow test portions to attain ambient temperature prior to analysis.

NOTE Additional sample handling recommendations are given in IP 558<sup>[4]</sup> and ASTM D7343.<sup>[5]</sup>

## 8 Apparatus preparation

### 8.1 Analyser

**8.1.1** Set up the analyser (6.1) in accordance with the manufacturer's instructions. Wherever possible, the instrument shall be continuously switched on to maintain optimum stability.

**8.1.2** Purge the optical system with helium (minimum 99 % purity) following the manufacturer's guidelines on flush time and flow rate to ensure the stability of measurements.

NOTE Analysis can be carried out without a helium purge, however the precision data were obtained using results only from instruments using a helium purge.

### 8.2 Sample cups

It is recommended to use disposable sample cups. 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, i.e. X-ray transparent film [(6.1 d)], for each run of verification and sampling analysis.