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SLOVENSKI STANDARD
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Naftni proizvodi - Določevanje žvepla v gorivih za motorna vozila - Ultravijolična fluorescenčna metoda (ISO/DIS 20846:2018)

Petroleum products - Determination of sulfur content of automotive fuels - Ultraviolet fluorescence method (ISO/DIS 20846:2018)

Mineralölerzeugnisse - Bestimmung des Schwefelgehaltes von Kraftstoffen - Ultraviolettfluoreszenz-Verfahren (ISO/DIS 20846:2018)

Produits pétroliers - Détermination de la teneur en soufre des carburants pour automobiles - Méthode par fluorescence ultraviolette (ISO/DIS 20846:2018)

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Petroleum products — Determination of sulfur content of automotive fuels — Ultraviolet fluorescence method

Produits pétroliers — Détermination de la teneur en soufre des carburants pour automobiles — Méthode par fluorescence ultraviolette

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Contents

Page

Foreword ..... **iv**
1 Scope **1**
2 Normative references **1**
3 Terms and definitions **2**
4 Principle **2**
5 Reagents and materials **2**
6 Apparatus **3**
7 Sampling **5**
8 Apparatus preparation **5**
9 Apparatus calibration and verification **6**
9.1 Multi-point calibration 6
9.2 One-point calibration 7
9.3 Verification 8
10 Procedure **8**
11 Calculation **9**
11.1 Using multi-point calibration 9
11.2 Using one-point calibration 10
11.3 Calculation 10
12 Expression of results **10**
13 Precision **11**
13.1 General 11
13.2 Repeatability, *r* *11*
13.3 Reproducibility, *R* *11*
14 Test report **12**
Bibliography **13**

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing Documents 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*.

This third edition cancels and replaces the second edition (ISO 20846:2011), which has been technically revised following a new interlaboratory study executed by CEN/TC 19/WG 27, *Elemental analysis,* that confirmed the method precision. The main changes however compared to the previous edition are as follows:

— In this edition the scope has been extended and now includes hydrotreated vegetable oil (HVO) and the synthetic fuel Gas To Liquid (GTL).

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.

Petroleum products — Determination of sulfur content of automotive fuels — Ultraviolet fluorescence method

WARNING — the use of this document may 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 the user of this document to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This document specifies an ultraviolet (UV) fluorescence test method for the determination of the sulfur content of motor gasolines containing up to 3,7 % (*m*/*m*) oxygen [including those blended with ethanol up to about 10 % (*V*/*V*)], diesel fuels, including those containing up to about 30 % (*V*/*V*) fatty acid methylester (FAME), having sulfur contents in the range 3 mg/kg to 500 mg/kg and synthetic fuels, such as Hydrotreated Vegetable Oil (HVO) and Gas To Liquid (GTL), having sulfur contents in the range of 3 mg/kg to 45 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 document. Halogens interfere with this detection technique at concentrations above approximately 3 500 mg/kg.

NOTE 1 Some process catalysts used in petroleum and chemical refining can be poisoned when trace amounts of sulfur-bearing materials are contained in the feedstocks.

NOTE 2 This test method can be used to determine sulfur in process feeds and can also be used to control sulfur in effluents.

NOTE 3 For the purposes of this document, the terms "% (*m*/*m*)" and "% (*V*/*V*)" are used to represent the mass fraction, μ, and the volume fraction, φ, of a material respectively.

NOTE 4 Sulfate species in ethanol do not have the same conversion factor of organic sulfur in ethanol. Nevertheless, sulfates have a conversion factor close to that of organic sulfur.

NOTE 5 It is preferable to check the nitrogen interference and to take it into account, especially when sulfur content is measured on diesel blended with cetane improver containing nitrogen. For example, alkyl nitrate, as 2-ethyl hexyl nitrate (EHN), added as cetane improver to diesel fuel shows an enhancing effect on sulfur content that can range from (0 to 1,7) mg/kg when 2 000 mg/kg EHN is added to diesel fuel containing 10 mg/kg sulfur.

2 Normative references

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wing 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 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3170, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

ISO 3675, *Crude petroleum and liquid petroleum products — Laboratory determination of density — Hydrometer method*

ISO 12185, *Crude petroleum and petroleum products — Determination of density — Oscillating U-tube method*

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

4 Principle

A hydrocarbon sample is injected into a UV fluorescence detector. The sample enters a high temperature combustion tube (1 000 °C to 1 100 °C), where the sulfur is oxidized to sulfur dioxide (SO_2) in an oxygen-rich atmosphere. Water produced during the sample combustion is removed and the sample combustion gases are exposed to UV light. The SO_2 absorbs the energy from the UV light and is converted to excited sulfur dioxide (SO_2*). The fluorescence emitted from the excited SO_2* as it returns to a stable state SO_2 is detected by a photomultiplier tube and the resulting signal is a measure of the sulfur contained in the sample.

5 Reagents and materials

5.1 Inert gas, argon or helium, high purity grade with a minimum purity of 99,998 % (*V*/*V*).

5.2 Oxygen, high purity grade with a minimum purity of 99,75 % (*V*/*V*).

CAUTION — Oxygen vigorously accelerates combustion.

5.3 Solvent

5.3.1 General

Use either that specified in 5.3.2 or 5.3.3, or a solvent similar to that occurring in the sample under analysis. Correction for sulfur contribution from solvents used in standard preparation and sample dilution is required. Alternatively, use of a solvent with non-detectable sulfur contamination relative to the unknown sample makes the blank correction unnecessary.

5.3.2 Toluene, reagent grade.

5.3.3 Isooctane, reagent grade.

CAUTION — Flammable solvents.

5.4 Sulfur compounds

5.4.1 General

Compounds with a minimum purity of 99 % (*m*/*m*). Examples are given in 5.4.2 to 5.4.4. Where the purity of these compounds is less than 99 % (*m*/*m*), the concentrations and nature of all impurities shall be established.

NOTE A correction for chemical impurity can be applied when the sulfur content is known with accuracy.

Certified reference materials (CRM) from accredited suppliers are suitable alternatives to the compounds listed in 5.4.2 to 5.4.4.

5.4.2 Dibenzothiophene (DBT), of molecular mass 184,26, with a nominal sulfur content of 17,399 % (*m*/*m*).

5.4.3 Dibutyl sulfide (DBS), of molecular mass 146,29, with a nominal sulfur content of 21,915 % (*m*/*m*).

5.4.4 Thionaphthene (Benzothiophene) (TNA), of molecular mass 134,20, with a nominal sulfur content of 23,890 % (*m*/*m*).

5.5 Sulfur stock solution

Prepare a stock solution of approximately 1 000 mg/l sulfur content by accurately weighing the appropriate quantity of sulfur compound (5.4) in a volumetric flask (6.9). Ensure complete dissolution with solvent (5.3). Calculate the exact sulfur concentration of the stock solution to the nearest 1 mg/l. This stock solution is used for the preparation of calibration standards. As an alternative procedure, a sulfur stock solution of approximately 1 000 mg/kg can be prepared by accurately weighing the appropriate quantity of sulfur compound (5.4) in a volumetric flask (6.9) and reweighing the volumetric flask once it has been filled to the mark with the solvent (5.3). Take precautions to ensure that evaporation of the solvent and/or sulfur compounds is not causing weighing errors.

The appropriate mass of sulfur compound described in 5.4.2 to 5.4.4 to add to the 100 ml flask is 0,574 8 g (DBT), 0,456 3 g (DBS) and 0,418 6 g (TNA).

NOTE The shelf life of the stock solution is approximately three months when stored at low temperature, typically in a refrigerator.

5.6 Calibration standards

Prepare the calibration standards by dilution of the stock solution (5.5) with the selected solvent (5.3).

Calculate the exact sulfur content of each calibration standard.

Calibration standards with a known sulfur concentration, in milligrams per litre, (or content, in milligrams per kilogram) can be obtained with a volume/volume dilution (or mass/mass dilution, respectively) of the stock solution at 1 000 mg/l (or 1 000 mg/kg respectively). Other practices are possible, but those mentioned above avoid any density correction.

New calibration standards should be prepared on a regular basis, depending upon the frequency of use and age. When stored at low temperature, typically in a refrigerator, the calibration standards with a sulfur content above 30 mg/kg (or mg/l) have a shelf life of at least one month. Below this sulfur content (30 mg/kg), the shelf life should be reduced.

5.7 Quality control samples

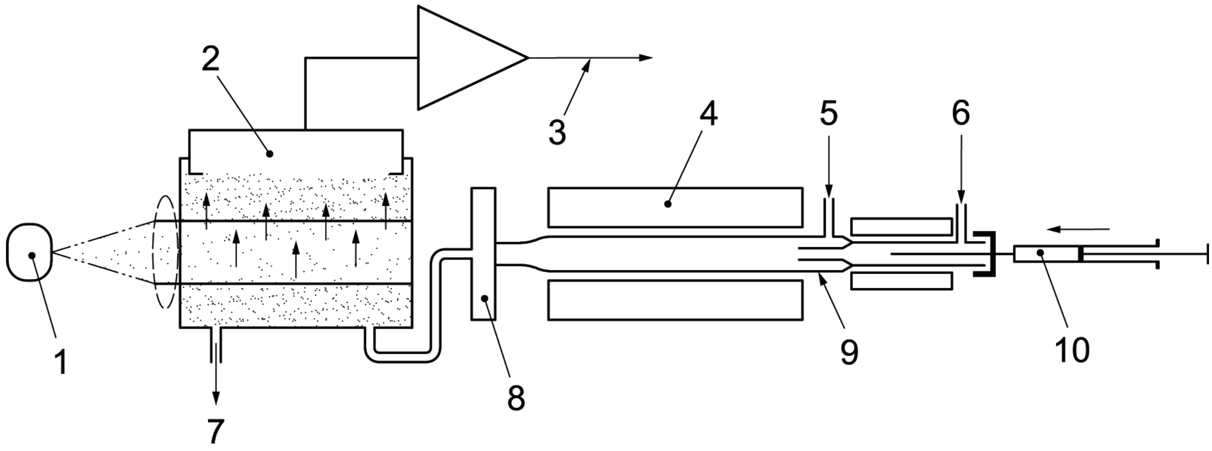
Quality control samples are stable samples representative of the materials being analysed, which have a sulfur content that is known by this test method over a substantial period of time. Alternatively, there are standard materials with a certified value commercially available. Prior to use, ensure that the material is within its shelf life.

5.8 Quartz wool

Follow the manufacturer's recommendations.

6 Apparatus

Figure 1 illustrates the basic pieces of the UVF.



Key

1 UV source
2 photomultiplier
3 output signal
4 furnace, 1 000 °C to 1 100 °C (6.1)
5 oxygen input
6 inert gas input
7 gases output
8 vapour drier (6.5)
9 quartz tube
10 microlitre syringe

Figure 1 — Synopsis of the apparatus

6.1 Furnace, comprising an electric device, capable of maintaining a temperature sufficient to pyrolyse all of the sample and oxidize all sulfur to sulfur dioxide (SO_2).

It can be set either in a horizontal or vertical position.

6.2 Combustion tube, of quartz, constructed to allow the direct injection of the sample into the heated oxidation zone of the furnace (6.1).

The combustion tube shall have side arms for the introduction of oxygen and carrier gas. The oxidation section shall be large enough to ensure complete combustion of the sample. It can be set either in a horizontal or vertical position.

6.3 Flow controllers, capable of maintaining a constant supply of oxygen and carrier gas.

6.4 Vapour drier, capable of removing water vapour formed during combustion prior to measurement by the detector (6.5).

6.5 UV fluorescence detector, selective and quantitative, capable of measuring light emitted from the fluorescence of sulfur dioxide by UV light.

WARNING — Exposure to excessive quantities of UV light is injurious to health. The operator must avoid exposing any part of his/her person, especially his/her eyes, not only to direct UV light, but also to secondary or scattered radiation that may be present.

6.6 Microlitre syringe, capable of accurately delivering between 5 µl to 50 µl quantities.

Follow the manufacturer’s instructions for determining the length of the needle required. For vertical injection, syringes with a polytetrafluoroethylene (PTFE) plunger are recommended.

