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Dimethyl ether (DME) for fuels — Determination of total sulfur, ultraviolet fluorescence method

Diméthylether (DME) pour carburants et combustibles — Détermination de la teneur en soufre total, méthode par fluorescence ultraviolet

ICS 71.080.60; 75.160.20

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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Foreword

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ISO 17198 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*, Subcommittee SC 4, *Classifications and specifications, WG 14, test methods*.

Introduction

In general, large amount of DME in the international trade and domestic transportation may be executed using sea and/or various land transportations. From the feed stock of synthesis gas for DME production and throughout the loading and transportation, there may be a risk of increasing sulfur contents.

Any sulfur compounds in DME used for, contributes to SO_x emissions. It can also cause corrosion in equipments. Therefore, sulfur content shall be tested accurately in process feeds, in finished products, as well as for compliance determinations required by regulatory authorities. It is common practice to analyze the sulfur, either by Ultraviolet Fluorescence or by Oxidative Microcoulometry .

This International Standard specifies the procedure of test by Ultraviolet Fluorescence Method.

Dimethyl ether (DME) for fuels — Determination of total sulfur — Ultraviolet fluorescence method

1 Scope

This International Standard specifies the procedure of test for the sulfur content in DME for fuels by the ultraviolet (UV) fluorescence method. This procedure is applicable to determine the amount of total sulfur up to the value specified in ISO 16861.

This test method will not measure sulphur that is not volatile under the practical conditions of the test, namely room temperature and atmospheric pressure.

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 CD16861: Di-methyl ether (DME) for fuels -- Specifications

ISO 29945: Refrigeration non-petroleum based liquefied gaseous fuels – Dimethyl Ether(DME) –
Method of manual sampling on shore terminals

ISO 5725-2: Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard.

3 Principle

A DME sample is directly injected into a UV fluorescence detector. The sample enters into a high-temperature combustion tube (1000°C to 1100°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 ultraviolet (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.

4 Reagents and materials

4.1 Inert gas

Inert gas, argon or helium, of high purity grade with a minimum purity of 99.998 volume %.

4.2 Oxygen

Oxygen, of high purity grade with a minimum purity of 99.75 volume %.

4.3 Solvent

4.3.1 General

Use either the solvent specified in 4.3.2 or 4.3.3 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.

4.3.2 n-Hexane, reagent grade.

4.3.3 Toluene, reagent grade.

4.4 Sulfur compounds

4.4.1 General

Compounds with a minimum purity of 99 mass %. Examples are given in 4.4.2 to 4.4.5. Where the purity of these compounds is less than 99 mass %, the concentrations and nature of all impurities are to be established. Certified reference materials from accredited suppliers are suitable alternatives to the compounds listed in 4.4.2 to 4.4.5.

4.4.2 Dibutyl sulfide (DBS)

4.4.3 Dibutyl disulfide (DBDS)

4.4.4 Dibenzothiophene (DBT)

4.4.5 Thionaphthene (benzothiophene) (TNA)

4.5 Sulfur stock solution

Prepare a stock solution of sulfur content approximately 1000 mg/l by accurately weighing the appropriate quantity of sulfur compound (5.4) in a volumetric flask (6.9). Ensure complete dissolution with solvent (5.4). Calculate the exact sulfur concentration of the stock solution to the nearest 1mg/l. This stock solution is used for the preparation of calibration standards. As an alternative procedure, a sulfur stock solution of approximately 1000 mg/kg can be prepared by accurately weighing the appropriate quantity of sulfur compound (5.4). Take precautions to ensure that evaporation of the solvent and/or sulfur compounds is not causing weighing errors.

4.6 Calibration standards

Prepare the calibration standards by dilution of the stock solution (4.5) with the selected solvent (4.3). 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 (or mass/mass, respectively) dilution of the stock solution at 1000 mg/l (or milligrams per kilogram, 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 at least a one month use of life. Below this sulfur content (30 mg/kg), the shelf life should be reduced.

4.7 Quality control samples

These are stable samples representative of the materials being analysed, that 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. Ensure before use that the material is within its shelf life.

5 Apparatus

5.1 Furnace

Furnace, comprising an electric device, capable of maintaining a temperature sufficient to pyrolyse all of the sample and oxidize all sulfur dioxide (SO_2). Follow manufacturer’s direction for the setting of the temperature.

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

5.2 Combustion tube

Combustion tube, of quartz, constructed to allow the direct injection of the sample into the heated oxidation zone of the furnace (5.1).

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.

5.3 Flow controllers

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

5.4 Vapour dryer

Vapour drier, capable of removing water vapour formed during combustion prior to measurement by the detector (5.5).

5.5 UV Fluorescence detector

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

5.6 Microsyringe

Microsyringe, capable of accurately delivering between 5 µl and 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.

5.7 Sample inlet system

Sample inlet system, positioned either vertically or horizontally. It shall consist of a direct-injection inlet system capable of allowing the quantitative delivery of the material to be analysed into an inlet carrier stream which directs the sample into the oxidation zone at a controlled and repeatable rate. A syringe drive mechanism, which discharges the sample from the microsyringe at a constant rate of approximately 1 µl/s maximum, is required.

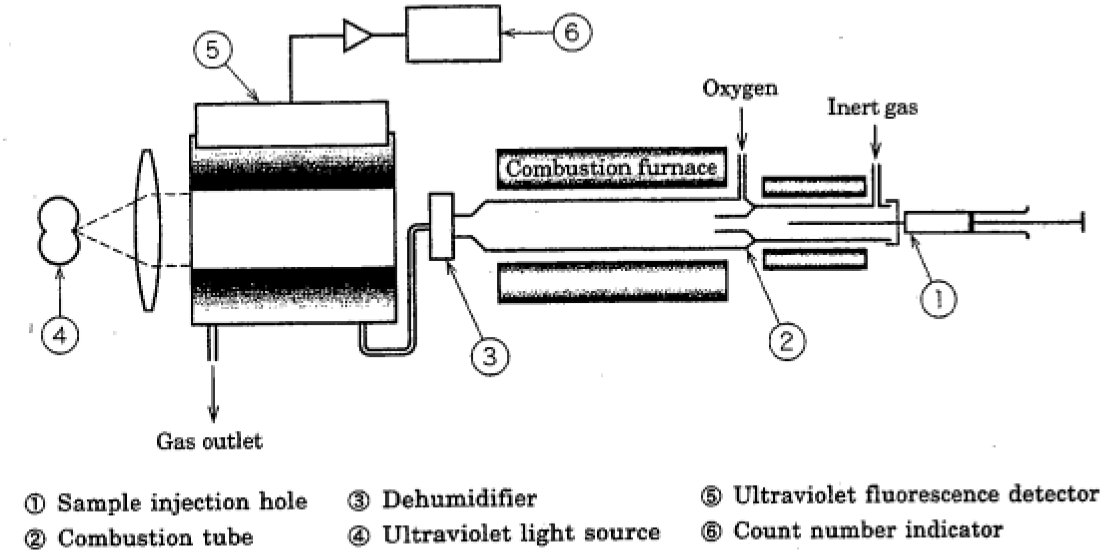

Figure 1 Test apparatus for ultraviolet fluorescence method (example)

5.8 Balance

Balance, capable of weighing with an accuracy of at least 0,1 mg.

5.9 Volumetric flasks

Volumetric flasks, Class A one-mark volumetric flasks, conforming to ISO 1042, of appropriate capacities, including 100 ml, for the preparation of sulfur stock solution (4.5) and calibration standards(4.6).

6 Procedures

6.1 Apparatus preparation

6.1.1

Assemble the apparatus and check for leaks according to the manufacturer’s instructions.

6.1.2

Adjust the inlet pressure and flow rate of each gas according to the manufacturer’s instructions.

6.1.3

Refer to the manufacturer’s instructions to set the temperature of the furnace (6.1) high enough to ensure all sulfur pyrolysis and oxidation, typically 1100°C in the case of a one-temperature-zone furnace or 750°C for pyrolysis, and 1000°C to 1100°C for oxidation in the case of a two-temperature-zone furnace.

6.1.4

Adjust the instrument sensitivity and baseline stability, and perform instrument blanking procedures following the manufacturer’s guidelines. Ensure that the UV light is stable before measurement.

NOTE For the UV light, a warm-up time of at least 30 min is usually required.