INTERNATIONAL STANDARD

**ISO
17198**

First edition
2014-11-15

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

DME comme carburant ou combustible — Détermination de la teneur en soufre total — Méthode par Fluorescence Ultraviolet

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Foreword

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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 on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 28, *Petroleum products and lubricants*, Subcommittee SC 4, *Classifications and specifications*.

Introduction

In general, large amounts of DME in the international trade and domestic transportation can 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 is a risk of increasing sulfur contents.

Any sulfur compounds in DME contributes to SO_x emissions. It can also cause corrosion in equipment. Therefore, sulfur content is tested accurately in process feeds, in finished products, as well as for compliance determinations required by regulatory authorities. It is common practice to analyse 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

WARNING — The use of this International Standard can 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 a procedure of test for the sulfur content in dimethyl ether (DME) used as fuel 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 sulfur that is not volatile under the practical conditions of the test, namely room temperature and atmospheric pressure.

NOTE   The precision of this method has been studied for a limited set of samples and content levels by a limited amount of labs. It allows establishment of a quality specification of DME but cannot be considered as a full precision determination in line with the usual statistical methodology as in ISO 4259.

2   Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 16861, *Petroleum products — Fuels (class F) — Specifications of dimethyl ether (DME)*

ISO 29945, *Refrigerated non-petroleum-based liquefied gaseous fuels — Dimethylether (DME) — Method of manual sampling onshore terminals*

3   Principle

A DME sample is directly injected into a UV fluorescence detector. The sample enters into 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 ultraviolet (UV) light. The SO_2 absorbs the energy from the UV light and is converted to excited 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**, argon or helium, of high purity grade with a minimum purity of 99,998 volume %.

4.2   **Oxygen**, of high purity grade with a minimum purity of 99,75 volume %.

4.3 Solvent.

Use either the solvent specified in 4.3.1 or 4.3.2 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.

4.3.1   *n*-hexane, reagent grade.

4.3.2   Toluene, reagent grade.

4.4   Sulfur compounds, compounds with a minimum purity of 99 mass %. Examples are given in 4.4.1 to 4.4.4. 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 4.4.1 to 4.4.4.

4.4.1   Dibutyl sulfide (DBS).

4.4.2   Dibutyl disulfide (DBDS).

4.4.3   Dibenzothiophene (DBT).

4.4.4   Thionaphthene (benzothiophene) (TNA).

4.5   Sulfur stock solution.

Prepare a stock solution of sulfur content approximately 1 000 mg/l by accurately weighing the appropriate quantity of sulfur compound (4.4) in a volumetric flask (5.9). Ensure complete dissolution with solvent (4.3). 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 (4.4). 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 mg/l or mg/kg, can be obtained with a volume/volume (or mass/mass) dilution of the stock solution at 1 000 mg/l or mg/kg. 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, 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).

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

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

5.5 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, 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, 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.
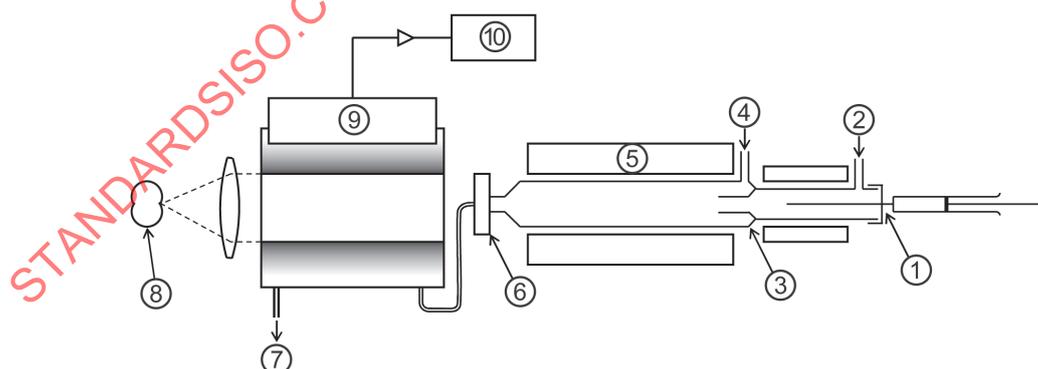
Key

1	sample injection hole	6	dehumidifier
2	inert gas	7	gas outlet
3	combustion tube	8	ultraviolet light source
4	oxygen	9	ultraviolet fluorescence detector
5	combustion furnace	10	count number indicator

Figure 1 — Test apparatus for ultraviolet fluorescence method (example)

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

5.9   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 (5.1) high enough to ensure all sulfur pyrolysis and oxidation, typically 1 100 °C in the case of a one-temperature-zone furnace or 750 °C for pyrolysis, and 1 000 °C to 1 100 °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.

6.2   Apparatus calibration and verification

6.2.1   Multi-point calibration

6.2.1.1   Prepare a series of calibration standards (5.6) by carrying out dilutions of the stock solution (5.5) with the selected solvent (5.3) to cover the range of operation (see Table 1 for examples). The number of calibration standards used in construction of the calibration curve can vary but it should not be less than four.

Table 1 — Examples of calibration standards

Sulfur content approximate value of sample mg/kg	Sulfur content of standards µg/L
0,5	1
1	2
2	4
5	10

6.2.1.2   Flush the microsyringe (5.6) several times with the solution to be analysed and ensure that the final liquid column in the syringe contains no bubbles.

6.2.1.3   Using one of the techniques described in 6.2.1.3.1 or 6.2.1.3.2, quantitatively analyse an appropriate sample size as specified by the manufacturer, prior to injection into the combustion tube for analysis.

NOTE   Injection of a constant or similar sample size for all materials analysed in a selected operating range promotes consistent combustion conditions.

6.2.1.3.1   For volumetric measurement, fill the syringe to the selected level and retract the plunger so that air is aspirated and the lower liquid meniscus falls on the 10 % scale mark. Record the volume of

liquid in the syringe. After injection, again retract the plunger so that the lower liquid meniscus falls on the 10 % scale mark and record the volume of liquid in the syringe. The difference between the two volume readings is the volume of sample injected.

NOTE   An automatic sampling and injection device can be used in place of the described manual injection procedure.

6.2.1.3.2   For mass measurement, weigh the syringe complete with a filled needle before injection, and the syringe and needle after injection, to determine the mass of the test portion injected.

NOTE   Mass measurement can be more accurate than the volume measurement for less volatile samples, if a balance with an accuracy of at least ±0,01 mg is used.

6.2.1.4   Once the appropriate sample size has been measured into the microsyringe, promptly and quantitatively deliver the sample into the apparatus. For direct injection, carefully insert the syringe into the inlet of the combustion tube (5.2) and the syringe drive. Allow time for sample residues to be burned from the needle (needle blank), Once a stable baseline has been re-established. Promptly start the analysis. Remove the syringe once the apparatus has returned to a stable baseline.

6.2.1.5   Construct each calibration curve by one of the techniques described in 6.2.1.5.1 to 6.2.1.5.2.

6.2.1.5.1   For manual construction, analyse the calibration standards and the blank three times using the procedure described in 6.2.1.2. to 6.2.1.4. Subtract the average blank response from each analysis of the standard before determining the average integrated response. Construct a curve by plotting average integrated detector response (y-axis) versus quantity, Q, in ng, of sulfur injected (x-axis). This curve should be linear with a correlation factor of at least 0,995.

Q is calculated using Formulae (1) and (2):

$$Q = m_c \times w_{sc} \tag{1}$$

or

$$Q = V_c \times x \rho_s \tag{2}$$

where

    m_c is the mass of the calibration standard injected, in ml, either measured directly or calculated from the measured volume injected and the density using Formula (3):

$$m_c = V_c \times D_c \tag{3}$$

where

    D_c is the density of the calibration standard at measurement temperature, in g/ml;

    V_c is the volume of the calibration standard injected, in mcl;

    W_{sc} is the sulfur content of the calibration standard, in mg/kg;

    ρ_s is the sulfur concentration of the calibration standard, in mg/.

6.2.1.5.2   If the apparatus features an internal calibration routine, analyse the calibration standards and the blank three times using the procedure described in 6.2.1.2 to 6.2.1.4. If blank correction is required and is not available (see 4.3), correct the analyser responses using the average response for each standard versus quantity, Q, in ng, of sulfur as obtained in 6.2.1.5.1. This curve should be linear with a correlation factor of at least 0,995.

6.2.1.6 A good practice consists of constructing a calibration curve in such a way that the sulfur content of the sample under analysis is in the middle of the calibration curve.

6.2.2 One-point calibration

6.2.2.1 Prepare a calibration standard (4.6) with a sulfur content close to that of the sample under analysis (±50 % maximum), by carrying out dilutions of the stock solution (4.5). A calibration standard with a sulfur concentration greater than 50 % from that of the sample can be used if the linearity of the apparatus has previously been checked. If necessary, the sulfur content of the calibration standard should be corrected by the sulfur content of the selected solvent (4.3).

NOTE   In order to measure the sulfur content of the selected solvent, the method of standards of the solvent gives satisfactory results.

6.2.2.2 Using the procedure described in 6.2.1.2 to 6.2.1.4., analyse a minimum of three times the calibration standard using an appropriate sample size as specified by the manufacturer.

6.2.2.3 Calculate a calibration factor, K_A, in number of counts per nanogram of sulfur using Formulae (4) and (5):

$$K_A = A_c / (m_c \times w_{sc}) \tag{4}$$

or

$$K_A = A_c / (V_c \times \rho_s) \tag{5}$$

where

A_c is the integrated detector response for the calibration standard, in number of counts;

m_c is the mass of the calibration standard injected, in mg, either measured directly or calculated from the measured volume injected and the density using Formula (6):

$$m_c = V_c \times D_c \tag{6}$$

where

D_c is the density of the calibration standard at measurement temperature, in g/ml;

V_c is the volume of the calibration standard injected, in mcl;

w_{sc} is the sulfur content of the calibration standard, in ml/kg;

ρ_s is the sulfur concentration of the calibration standard, in ml/l.

Calculate the average calibration factor and check that the standard deviation is within the accepted tolerance.

When the content of calibration standards is known in mg/kg, and volume injections are performed, a correction for the difference of density between standards and samples is necessary.

6.3 Verification

6.3.1 Check the calibration validity with a quality control sample of known sulfur content, at the beginning of a series of analyses and at least every 20 analyses during a long series of analyses.

6.3.2 Compare the results to the known values and associated uncertainties. The out-of-limit results shall be investigated for root cause(s).

Control limits are established from the laboratory statistical control charts, but initial values should be set before this happens. Limits of the repeatability of this method, or 0,7 times the reproducibility, are reasonable starting points.

6.4 Sampling and Measurement

Samples shall be taken as described in ISO 29945.

6.4.1 Procedure for weighing out of sample

The procedure for weighing out of the sample shall be as follows.

a) Preparation

For the sample cylinder which is prepared according to ISO 29945, as example shown in Figure 2, connect the needle valve to the sample cylinder outlet (liquid side) as given in figure and connect the sample cylinder to the intake opening of a gas collecting bag made of fluoropolymer film or the like through the three way valve made of polytetrafluoroethylene resin by using a stainless steel tube, an polytetrafluoroethylene resin tube, etc.
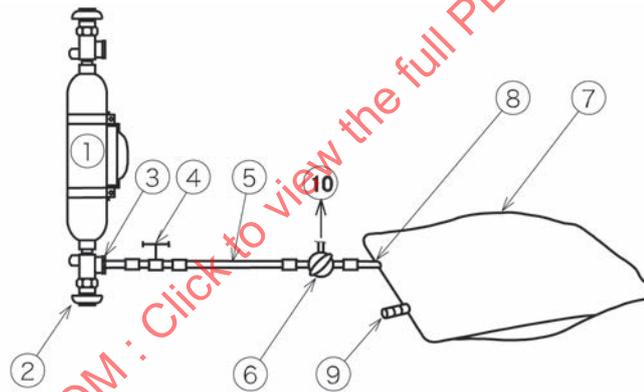
Key

1   sample cylinder
2   original valve
3   sample cylinder outlet
4   needle valve
5   tube of stainless steel, polytetraflouroethylene, etc. (within 50 cm length)
6   three-way clock
7   gas collecting bag (1 l to 5 l capacity)
8   intake opening for gas collecting bag
9   sampling port for sample gas (with a septum)
10 to vacuum pipe or aspirator

Figure 2 — Connection of sample cylinder to gas collecting bag (example)

b) Washing with sample

Gradually open the original valve of a sample cylinder, and regulate appropriately so that the bag does not inflate quickly. When the volume in the gas collecting bag becomes approximately 50 % to 70 %

of the tolerable volume, close the original valve, and exhaust the sample gas 3 min later. Perform this operation twice.

c) Weighing out of sample

Take a gasified sample into a gas collecting bag in the same way as in b). Wash a gas tight syringe two or three times with the sample gas through the septum of a sampling opening 3 min later after closing the original valve. Thereafter, weigh out the sample gas. Measure the weight of syringe before and after the injection.

6.4.2 Measurement of sample

6.4.2.1 Sample injection by gas tight syringe

Weigh out the quantity of the sample corresponding to the sulfur content approximate value of the sample according to the Table 2 into a gas tight syringe in accordance with 6.4.1 c), inject from the sample injection opening of a detector, and read the value displayed on a sulfur quantity indicator. However, allow the injection speed to be 0,2 ml/s to 2,0 ml/s.

Table 2 — Weighing out quantity of sample

Sulfur content approximate value of sample	Weighing out quantity
mass %	ml
0,000 1 or over to and excl. 0,010 0	10
0,010 0 or over up to and incl. 0,030	5

6.4.2.2 Use of automatic injection

The use of an automatic injection, by the analytic instrument, from the collecting gas bag can be used in place of the described manual injection using gas tight syringe in 6.4.2.1.

6.4.3 Using the procedure described in 6.2.1.2 to 6.2.1.4., analyse an appropriate sample size three times as specified by the manufacturer.

6.4.4 Inspect the combustion tube and other flow path components to verify complete oxidation of the test portion. If deposits are noted, follow the procedures given in 6.4.5 and 6.4.6.

6.4.5 If coke or soot is observed, clean any parts of the combustion tube in accordance with the manufacturer's instructions. After cleaning and/or adjustment, assemble the apparatus and check for leaks. Carry out a check on the calibration quality prior to reanalysis.

6.4.6 Use a reduced sample size or a reduction of injection rate, or both.

6.5 Calculation and result

6.5.1 Using multi-point calibration

For analysers calibration using a standard curve, calculate the sulfur content, S, of the sample, in mg/kg, using Formula (7):

$$S = \frac{22,4 \times B}{V \times \dfrac{273}{273+t} \times M} \tag{7}$$

where

B is the sulfur quantity obtained with the calibration curve, ng;

V is the sample injection quantity, ml;

t s the sample temperature, °C;

M is the mass per 1 mol of a sample, g/mol;

Y is the y-intercept of the standard curve, ng.

NOTE 1   The sample has to be in room temperature.

NOTE 2   M is 46,07 g/mol for DME.

6.5.2 Using one-point calibration

Calculate the sulfur content, S, of the sample, in mg/kg, using Formula (8):

$$S = \frac{22,4 \times A}{V \times \dfrac{273}{273+t}} M \times K_A \tag{8}$$

where

A is the integrated detector response for the sample, counts;

V is the sample injection quantity, ml;

t is the sample temperature, °C;

M is the mass per 1 mol of a sample, g/mol;

K_A is the calibration factor, counts/ng of sulfur.

NOTE 1   The sample has to be in room temperature.

NOTE 2 M is 46,07 g/mol for DME.

7 Precision

The provisional precision of this method, established during interlaboratory tests relating to DME sample with sulfur content of 2,41 mg/kg, and determined on the basis of statistical examination of interlaboratory test results, is shown in Table 3. Refer to Annex A for the report of the interlaboratory test.

NOTE   The emphasis of the interlaboratory study was to confirm that the sample analysed fulfils ISO 16861 specification or not, rather than to establish an analytical method applicable for a wide range. The reproducibility determined is only indicative and should not be considered as one established according to normal statistical procedures as in ISO 4259. The figures are provisional and further work in the future is intended to improve the estimation given.

— Repeatability, *r*: The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on nominally identical test material would, in the long run, in the normal and correct operation of the test method, exceed the value below in only one case in 20.

— Reproducibility, *R*: The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the long run, in the normal and correct operation of the test method, exceed the value below in only one case in 20.

Table 3 — Provisional precision

Dimensions in mg/kg

Component	Content	Repeatability, *r*	Reproducibility, *R*
Total sulfur	0 to 3,0	0,03 *X*	0,19 *X*
NOTE *X* is the mean of the measured value.			

8 Test Report

The test report shall include at least the following information:

a) a reference to this International Standard (i.e. ISO 17198:2014);

b) a reference to the UV sulfur analyser system;

c) all the necessary information for complete identification of the sample, for example

— date of sampling;

— place in the pipeline system at which the sample was taken;

d) the sampling method used (including the size and type of material of the high-pressure cylinder used);

e) sulfur content in the sample, in mg/kg, to one decimal point;

f) details of any deviation from the procedure specified.