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Dimethyl ether (DME) for fuels — Determination of impurities — Gas chromatographic method

Diméthylether (DME) pour carburants et combustibles — Détermination des impuretés — Méthode par chromatographie en phase gazeuse

ICS 71.080.60; 75.160.20

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 17196 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*, Subcommittee SC 4, *Classifications and specifications*.

This second/third/... edition cancels and replaces the first/second/... edition (), [clause(s) / subclause(s) / table(s) / figure(s) / annex(es)] of which [has / have] been technically revised.

Introduction

Throughout the manufacturing process, DME may contain some impurities. In addition, there is a possibility that DME may be contaminated during loading and transportation by sea and/or various land transportations. Examples of such impurities include methanol, water, carbon dioxide, ethyl methyl ether, sulfur, residues and so on.

Gas chromatography is recommended to analyze many kinds of vaporizable impurities.

Dimethyl ether (DME) for fuel – Determination of impurities – Gas chromatographic method

WARNING – The use of this International Standard may 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 describes the quantitative analysis method of the following components likely to be contained in DME by gas chromatography: methanol, CO, CO_2, methyl formate, ethyl methyl ether, and hydrocarbons up to C_4, in the concentration range specified in ISO CD16861.

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: Refrigerated non-petroleum-based liquefied gaseous fuels -- Dimethylether (DME) -- Method of manual sampling onshore 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

measurement method

ISO 6142: Gas analysis - Preparation of calibration gas mixtures - **Gravimetric** method

ISO 6143: Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures

ISO 7504: Gas analysis – Vocabulary

ISO 6975: Natural gas – Extended analysis – Gas – chromatographic method

3 Definitions

- Resolution: refer to ISO 6975

- Response: refer to ISO 6975

- Reference component: refer to ISO 6975

3.1 Components

DME, methanol, ethyl methyl ether, methyl formate, carbon dioxide, carbon monoxide, hydrocarbons up to C_4

3.2 Hydrocarbons (up to C_4)

Components such as,

Ethane (C_2H_6), ethylene (C_2H_4), propane(C_3H_8), propylene(C_3H_6), i-butane(i-C_4H_{10}), n-butane(n-C_4H_{10}), i-butene (i-C_4H_8), 1-butene (1-C_4H_8), trans-2-butene (trans-2- C_4H_8), cis-2-butene (cis-2- C_4H_8), 1,3-butadiene (1,3-butadiene).

3.3 Working-reference gas mixture WRM:

Mixtures which are used as working standards for regular calibration of the measuring system.

NOTE: WRM gas mixtures may be prepared by gravimetric method in accordance with ISO 6142 or certified and validated by comparison with gas mixtures in accordance with ISO 6143

4 Principle

The components to be determined in a gaseous sample are separated by gas chromatography and compared with calibration data obtained under the same set of conditions.

The components are separated using packed or open tubular columns in a gas chromatograph and detected by TCD or FID or FID with methanizer.

5 Analysis and analytical requirements

5.1 Apparatus and materials

5.1.1 Analytical system

The analytical system shall consist of gas chromatograph and appropriate data handling system.

NOTE: Examples of analytical systems and conditions are informatively proposed in this standard (see Annex A and Annex B)

The gas-chromatographic unit may consist of one or more gas chromatographs capable of isothermal and/or temperature-programmed operation and equipped with a TCD and an FID and a sample heated transfer and introduction system. A methanizer is optional

Sample is preferably transferred as a gas phase to the injection system thanks to a constant volume system according to the annexes.

If sample is transferred as a gas phase, a specific procedure to allow full vaporization of liquid sample is required (see 6.2.1)

Liquid sampling valve may also be used to inject the sample in a liquid phase.

5.1.2 Reference gas mixtures

5.1.2.1 Working reference gas mixture

The concentration of each component in the WRM shall be within the tolerances given in table 1 relative to the maximum value allowed in the specification ISO 16861

WRM for following components should be prepared.

CO, CO_2, methanol, methyl formate, propane, butane, ethyl methyl ether

WRM for other hydrocarbons up to C_4 maybe prepared.

Note: Standard reagents or standard gas for ethyl methyl ether may not be widely available in the market. However, it is necessary to obtain such mixture to perform test methods described in this standard.

Example of WRM is shown in Annex C.

Table 1 - Tolerance between concentrations of components in the WRM and sample

component concentration allowed in specification ISO 16861 (mass %)	Deviation of component concentration in WRM(% relative to value specified in ISO 16861)
Up to 0,1	± 50
0,1 to 1	± 25

5.1.2.2 Control gas

A control gas is a high-pressure gas mixture containing all the components present in the working-reference gas mixture. A sample gas mixture having a composition closely related to the WRM may be used.

A control gas is used for the determination of the mean (p) and standard deviation (a) of the concentrations of the components detected.

5.2 Resolution

The resolution between two adjacent peaks for each component shall not be less than 2.

In the event that a valve switching is performed in multicolumn analysis, the resolution between the peak of the component eluted before switching the valve and the peak of the component that would be eluted without the valve switching shall not be less than 4

If the resolution is unsatisfactory, the selection of chromatograph columns and/or the analytical conditions should be optimized until the expected resolution is obtained.

6 Procedures

6.1 Setting up the analytical system

Set up all the analytical system in accordance with the manufacturer's instructions and the analytical methods chosen.

We must avoid condensation and sorption in the sampling system. The sample cylinder and the transfer line and all the lab equipment shall be in a well air-conditioned room or the sample cylinder and transfer line shall be heated to at least 10°C above the greater of the sampling temperature or ambient temperature. If necessary, use a heated vaporiser to ensure complete vaporisation. In case of gas phase transfer and injection, special precautions shall be taken at any spot in the system where pressure reduction occurs.

6.2 Sample preparation

Samples shall be taken as described in ISO 29945.

Note: Since DME is a liquefied gas, depending on the filling level and pressure, CO and CO_2 may be more concentrated in the vapor phase of the sample container. The CO and CO_2 concentration in the vapor phase can be calculated if the distribution coefficient of CO and CO_2 in liquid phase and vapor phase is known at given pressure. See annex E for distribution coefficient.

6.3 Injection

Either of the three following procedures may be used :

6.3.1 Gas phase injection

Connect a sample cylinder to the sample injector, replace by letting the sample gas flow into the sample measuring pipe. Purge the transfer line and the sampling loop for a sufficient period. And then inject the sample gas into the column by switching the passage of sample injector and measure the peak area.

Note that the sample should be taken from the liquid phase of the sample cylinder. It is necessary to take measures to ensure complete evaporation of the sample, and also measures should be taken to avoid condensation of the sample.

For an example of the gas phase sample injection, refer to the practices in Annex A.

6.3.2 Liquid injection with liquid injection valve

If liquid injection valve is used, the sample should be kept under pressure to avoid evaporation, and hence ensure repeatable injection. Ensure liquid DME is flowing at the vent of the liquid sampling valve before injection into the column.

7 Calibration, calculation and control charts

7.1 Calibration

Analysis of the WRM according to the present procedure is carried out periodically or if required by control chart inspection (see 7.3)

7.2 Calculation

Obtain the concentration (volume %) of each component in sample gas according to the following formula (1). Next, calculate the content (mass %) of each composition to four decimal according to the following formula (2) in order to convert volume % to mass % and round off to three decimal places.

(1) $$Cvi = \frac{Ai \times Pi}{Asi}$$

Where:

Cvi is calculated concentration (volume %) of compound *i* in the sample

Ai is the peak area of compounds *i* in the sample

Asi is the peak area of compounds *i* in the last analysis of the WRM

Pi is the concentration (volume %) of compounds *i* in the last analysis of the WRM

(2) $$Cwi = \frac{Cvi \times Mi}{\sum_{i=1}^{n} (Cvi \times Mi)}$$

Where:

Cwi is calculated concentration (mass %) of compound *i* in the sample

Mi is molecular mass (g) of compounds *i* in the sample

n is total number of compounds

7.3 Control charts

Refer to ISO 6975 for the detailed description of control charts.

Carry out a control gas (5.1.2.2) analysis with each batch of sample. Its composition is unvarying and so the results of this analysis can be used as an indication as to whether the method is no longer working satisfactorily or recalibration is necessary, or both.