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Dimethyl ether (DME) for fuels — Determination of water content — Karl Fischer titration method

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National foreword

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INTERNATIONAL STANDARD

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Dimethyl ether (DME) for fuels — Determination of water content — Karl Fischer titration method

Diméthylether (DME) pour carburants et combustibles — Détermination de la teneur en eau — Méthode par titrage Karl Fischer

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Foreword

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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 international trade and domestic transportation can be executed using sea and/or various land transportations. Throughout loading and transportation, there is a risk of increasing the DME's water content.

DME is soluble in water and the amount of water contained in the DME gives significant detrimental influence when it is used as fuel.

Accordingly, water content in DME has to be analysed accurately using recognized procedures by the parties concerned.

In this International Standard, one of the most common practices to be applied to analysis of water content is standardized.

INTERNATIONAL STANDARD **ISO 17197:2014(E)**

Dimethyl ether (DME) for fuels — Determination of water content — Karl Fischer titration 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 specifies a procedure of test for the amount of water content in DME used as fuel by the Karl Fischer titration method. This procedure is applicable to determine the amount of water up to the value specified in ISO 16861.

This test method is intended for use with commercially available coulometric (or volumetric) Karl Fischer reagents and for the determination of water in DME additives, lube oils, base oils, automatic transmission fluids, hydrocarbon solvents, and other petroleum products. By proper choice of the sample size, this test method can be used to determine water from mg/kg (ppm) to percent level concentrations.

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

3 Principle

A gaseous sample of DME is bubbled into the titration vessel of a coulometric (or volumetric) Karl Fischer apparatus. The titration is then performed until all of the water has been titrated, the end point is detected by an electrometric end point detector, and the titration is terminated. Based on the stoichiometry of the reaction, 1,0 mol of iodine reacts with 1,0 mol of water; thus, the quantity of water is proportional to the quantity of Karl Fisher reagent used.

4 Reagents and materials

4.1 Sample solvent, reagent grade.

Use methanol (anhydrous) with minimum purity 99,9 mass % and maximum water content 0,1 mass % (and preferably less than 0,05 mass %).

This water content could be achieved by dissolving 24 g of magnesium metal turnings in 200 ml of methanol (the reaction could be vigorous). When the reaction is completed, add 3 l of methanol. Reflux for 5 h. Distill directly into the container in which the 99,9 mass % methanol is to be kept. Vent the system through a drying tube during the distillation.

4.2 Coulometric Karl Fischer reagent.

Use standard, commercially available reagents for coulometric Karl Fischer titrations.

4.2.1 Anode solution.

Use a standard, commercially available anode Karl Fischer solution. A newly made solution should be used.

4.2.2 Cathode solution.

Use a standard, commercially available cathode Karl Fischer solution. A newly made solution should be used.

4.3 Volumetric Karl Fischer reagent.

Use standard, commercially available, pyridine-free Karl Fischer reagents for volumetric titrations (one or two components). Use as described in 4.1.

4.3.1 One component.

Use a commercial volumetric Karl Fischer reagent. Fresh Karl Fischer reagent shall be used (alternatively, the solution should be standardized or calibrated each time it is used).

4.3.2 Two components.

Use commercial volumetric Karl Fischer reagent. Mix the two reagents (part 1 and part 2) just before using. The solution should be standardized and calibrated as soon as possible.

4.3.3 Methanol (anhydrous).

4.4 Molecular sieve.

A ball- or cylindrical-shaped molecular sieve shall be used. All vented ends of the system shall be through drying tubes filled with this molecular sieve. Alternatively, anhydrous calcium chloride could be used.

4.5 Water.

Distilled water or water of equivalent purity shall be used.

5 Apparatus

5.1 Karl Fischer apparatus (coulometric or volumetric), using electrometric end point.

A number of automatic coulometric and volumetric Karl Fischer titration assemblies consisting of titration cell, platinum electrodes, magnetic stirrer, and a control unit are available on the market. Instructions for operation of these devices are provided by the manufacturers and are not described herein. A sample is introduced using a stainless steel needle for gas bubbling; the length can be about 200 mm and the diameter can be about 1 mm.

5.2 Pressure gas cylinder.

Samples are most easily added to the titration vessel by means of double-valve pressurized gas cylinders (size is up to 100 ml, tested pressure not less than 3,0 MPa) that the mass could be measurable. The sample should be delivered from the bottom of the cylinder.

5.3 Electronic balance.

The mass of the samples are determined by means of a top loading electronic balance with an accuracy of at least 1,0 mg and with capacity that covers the mass of double-valve pressurized gas cylinders filled with the sample. The sample mass is concluded by the difference between the cylinder mass before and after the test (after excluding the purge sample quantity).

6 Sampling and sample handling

6.1 Samples shall be taken as described in ISO 29945.

6.2 Test Specimen: the aliquot obtained from the laboratory sample for analysis by this test method. Once drawn, use the entire portion of the test specimen in the analysis.

6.3 Select a test specimen size from 10 g to 20 g.

7 Preparation of apparatus

7.1 Follow the manufacturer's directions for preparation and operation of the titration apparatus.

7.2 Seal all joints and connections to the vessel to prevent atmospheric moisture from entering the apparatus.

7.3 Add the sample solvent into the titration vessel to the level that is recommended by the manufacturer. Prepare the Karl Fischer reagent as described in 4.2 or 4.3.

For coulometric titration, add the Karl Fischer anode solution to the anode (outer) compartment. Add the solution to the level recommended by the manufacturer. Add the Karl Fischer cathode solution to the cathode (inner) compartment. Add the solution to a level 2 mm to 3 mm below the level of the solution in the anode compartment.

7.4 Turn on the apparatus and start the magnetic stirrer for a smooth stirring action. Allow the residual moisture in the titration vessel to be titrated until the end point is reached. Do not proceed beyond this stage until the background current (or background titration rate) is constant and less than the maximum recommended by the manufacturer of the instrument.

7.5 Install the needle to the double-valve gas cylinder. Stick the needle of the cylinder to the titration flask and fix the cylinder. The needle shall be rolled with tissue paper or threaded into a silicone rubber plate to prevent dew condensation water from mixing into the titration flask.

7.6 Open the liquid valve of the sample cylinder slowly and adjust the gas flow rate in the range of 0,5 g/min to 2,0 g/min. Be sure that the gas doesn't generate foam or overflow. The needle shall be below the liquid surface, with at least 3,0 cm to allow the water content in the bubbled gas to be extracted in the solvent.

7.7 Allow the residual moisture in the titration vessel to be titrated until the end point is reached again. The system now is ready for sample titration. Disconnect the sample cylinder and measure the mass and record as the "initial sample mass".

8 Calibration and standardization

8.1 Standardize the Karl Fischer reagent at least once daily.

8.2 Add enough solvent to the clean, dry titration vessel to cover the electrodes. The volume of solvent depends on the size of the titration vessel. Seal all openings to the vessel and start the magnetic stirrer for a smooth stirring action. Turn on the indicating circuit and adjust the instrument to give a reference end point.

8.3 For the coulometric technique, follow the manufacturer instructions for instrument calibration.

8.4 For the volumetric technique, standardize the Karl Fischer reagent with water by one of the following methods.

— From a water-filled pipette or syringe previously measured with mass to the nearest 0,1 mg, add 1 drop of water (about 20 mg) to the sample solvent at end-point conditions and measure the mass of the syringe. Record the mass of the water added. Titrate the water with Karl Fischer reagent added from the pipette or syringe until a steady end point is reached for at least 30 s. Record to the nearest 0,01 ml the volume of the Karl Fischer reagent needed to reach the end point.

— Fill a 10 µl syringe with water taking care to eliminate air bubbles, wipe the needle with tissue paper to remove any residual water from the needle, and accurately determine the mass of syringe plus water to 0,1 mg. Add the contents of the syringe to the sample solvent in the cell which has been adjusted to the end point ensuring that the tip of the needle is below the surface of the sample solvent. Reseal the vessel immediately. Remove any solvent from the needle by wiping it with tissue paper and measure the mass of the syringe to 0,1 mg. Titrate the water with Karl Fischer reagent as in 4.2 or 4.3.

8.5 Calculate the water equivalence of the Karl Fischer reagent using Formula (1).

$$F = W/T \qquad (1)$$

where

F is the water equivalence of the Karl Fischer reagent, in mg/ml;

W is the water added, in mg;

T is the reagent required for titration of the added water, in ml.

8.6 Duplicate values of water equivalence should agree within 2 % relative. If the variation between the two titrations is greater than 2 % relative, discard the contents of the titration vessel. Introduce a further portion of sample solvent into the vessel and repeat the standardization procedure. If the titrations for two further portions of water still vary by more than 2 %, it is likely that either the Karl Fischer reagent or the sample solvent, or both, have aged. Replace these with fresh reagents and repeat the procedure for calibration and standardization.

8.7 Determine and record the mean water equivalence value.

9 Procedure

9.1 Add newly made solvents to the anode and cathode compartments of the titration vessel and bring the solvent to end-point conditions as described in Clause 6.

9.2 Add the dimethyl ether test specimen to the titration vessel using the procedures described in 8.3 and 8.4, considering the following.

— Estimate the time that is required to consume the desired sample mass described in 6.3.

- After bubbling the sample in the titration vessel, close the bottom sample valve and wait until all sample trapped in the connection joints complete the bubbling in the titration vessel.
- Disconnect the sample cylinder and measure the mass and record that mass as the “final sample mass”.

9.3 Allow the instrument to start automatic titration until all moisture in the titration vessel has been titrated and the same end point is reached. Do not proceed beyond this stage until the background current (or background titration rate) is constant and less than the maximum recommended by the manufacturer of the instrument.

9.4 When the background current or titration rate returns to a stable reading at the end of the titration as discussed in Clause 7, additional specimens can be added as in 9.2 to 9.3.

9.5 Replace the solutions when one of the following occurs and then repeat the preparation of the apparatus as in Clause 7.

- Persistently high and unstable background current.
- Phase separation in the anode compartment or oil coating the electrodes.
- The total DME added to the titration vessel exceeds one-quarter of the volume of solution in the anode compartment.
- The solutions in the titration vessel are greater than one week old.
- The instrument displays error messages that directly or indirectly suggest replacement of the electrolytes (see instrument operating manual).
- The result of a 10 µl injection of water is outside 10 000 µg ± 200 µg.

10 Calculation

10.1 For the Coulometric technique, calculate the water concentration, in mg/kg or µg/g, of the sample using Formula (2).

$$\text{Water, mg/kg (or µg/g)} = W_1/W_2 \tag{2}$$

where

W_1 is the mass of water titrated, in mg or µg (as appropriate);

W_2 is the mass of sample used, in kg or g (as appropriate).

10.2 For the volumetric technique, calculate the water concentration, in mass %, of the sample using Formula (3).

$$\text{Water, mass \%} = \frac{C \times F}{10 \times W} \qquad (3)$$

where

C is the Karl Fisher reagent required to titrate the water content in the sample, in ml;

F is the water equivalence of the Karl Fisher reagent, in mg/ml;

W is the sample mass used, in g;

10 is the factor for converting to percentage.

11 Report

The test report shall include at least the following information:

a) a reference to this International Standard (i.e. ISO 17197:2013);

b) a reference to the Karl Fischer 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) the water concentration in mass %, to three decimal places;

f) if possible, the precision of the determined water concentrations of the sample, including the number of determinations;

g) the details of any deviation from the procedure specified.

12 Precision

The provisional precision of this method, established during interlaboratory tests relating to a DME sample with water content of 0,034 3 mass % and determined on the basis of statistical examination of interlaboratory test results is shown in Table 1. 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.

Refer to ISO 5725-2 for the detailed definition of repeatability, *r,* and reproducibility, *R*.

Table 1 — Provisional precision

Dimensions in mass %

Component	**Content range**	**Repeatability**, *r*	**Reproducibility**, *R*
Water	0 to 0,030	0,023 *X*	0,047 *X*
NOTE *X* is the mean value of the measured data.			

Annex A
(informative)

Report of the interlaboratory tests

A.1 Precision

A.1.1 Outline of the test

A repeatability standard deviation and a reproducibility standard deviation were calculated from results of a round robin test which was carried out with one sample by six laboratories.

A.1.2 Round robin test results

The precision was evaluated by Cochran's test and Grubbs' test prescribed in ISO 5725-2, then the repeatability standard deviation and the reproducibility standard deviation were calculated. The test results are shown in Table A.1. These values were determined from a level experiment involving six laboratories with 0,034 3 mass % of sample, in which no stragglers were detected.

Table A.1 — Round robin test results (water)

Dimensions in mass %

Laboratory	1st	2nd	3rd	4th	5th	Average	Standard deviation	Number of tests
L1	0,033 55	0,035 09	0,035 97	0,034 40	0,034 99	0,034 80	0,000 90	5
L2	0,034 64	0,034 31	0,035 12	—	—	0,034 69	0,000 41	3
L3	0,034 19	0,034 92	0,035 99	—	—	0,035 03	0,000 91	3
L4	0,031 9	0,032 4	0,031 3	—	—	0,031 9	0,000 6	3
L5	0,034 14	0,034 77	0,036 10	0,036 97	0,035 69	0,035 54	0,001 11	5
L6	0,032 63	0,033 20	0,032 65	—	—	0,032 83	0,000 32	3
The general mean	0,034 3							
Total number of tests	22							
Repeatability standard deviation	0,000 8							
Reproducibility standard deviation	0,001 6							

A.1.3 Provision of precision

Normally, results measured by plural level samples should be used for calculation of precision; only one level sample was used in this round robin test because of limited samples and time. Therefore, tolerance of repeatability and the reproducibility standard deviation were estimated assuming that the repeatability and the reproducibility standard deviation calculated by the test results are linear. The estimated tolerance of repeatability and the reproducibility standard deviation is shown in Figure A.1.

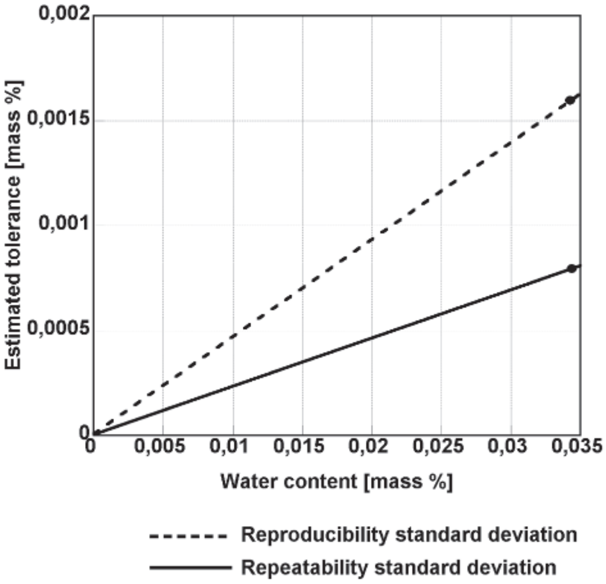

Figure A.1 — Estimated tolerance of repeatability and the reproducibility standard deviation

Bibliography

[1] ISO 760, *Determination of water — Karl Fischer method (General method)*

[2] ISO 4259, *Petroleum products — Determination and application of precision data in relation to methods of test*

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