BS ISO 17196:2014

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

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National foreword

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The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum Testing and Terminology.

A list of organizations represented on this committee can be obtained on request to its secretary.

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INTERNATIONAL STANDARD

ISO 17196

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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

Reference number
ISO 17196:2014(E)

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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).

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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*.

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Introduction

Throughout the manufacturing process, impurities can generate in the dimethyl ether (DME). In addition, there is a possibility that DME becomes 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 analyse many kinds of vaporizable impurities.

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INTERNATIONAL STANDARD **ISO 17196:2014(E)**

Dimethyl ether (DME) for fuels — Determination of impurities — Gas chromatographic 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 methanol, CO, CO_2, methyl formate, ethyl methyl ether, and hydrocarbons up to C_4, in DME used as fuel by the gas chromatography method. This procedure is applicable to determine the amount of methanol, CO, CO_2, methyl formate, ethyl methyl ether, and hydrocarbons up to C_4, up to the value specified in ISO 16861.

NOTE The precision of this method has been studied for a limited set of samples and content levels by a limited number 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 6975, *Natural gas — Extended analysis — Gas-chromatographic method*

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

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

3 Terms and definitions

For the purposes of this document, the following terms and definitions given in ISO 6975 and the following apply.

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), and 1,3-butadiene (1,3-butadiene)

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3.3

working reference gas mixture

WRM

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

Note 1 to entry: WRM can 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 a gas chromatograph and an appropriate data handling system.

NOTE Examples of analytical systems and conditions are informatively proposed in this International Standard. See Annex A and Annex B.

The gas-chromatographic unit can 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.

The sample is preferably transferred as a gas phase to the injection system through a constant volume system according to the annexes.

If the sample is transferred as a gas phase, a specific procedure to allow full vaporization of liquid sample is required (see 6.3.1).

A liquid sampling valve can 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 in ISO 16861.

WRM for the following components should be prepared: CO, CO_2, methanol, methyl formate, propane, butane, and ethyl methyl ether.

WRM for other hydrocarbons up to C_4 can be prepared.

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

Example of a WRM is shown in Annex C.

Table 1 — Tolerance between concentrations of components in the WRM and the 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 can 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.

Condensation and sorption in the sampling system shall be avoided. 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 vaporizer to ensure complete vaporization. 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 might be more concentrated in the vapour phase of the sample container. The CO and CO_2 concentration in the vapour phase can be calculated if the distribution coefficient of CO and CO_2 in liquid phase and vapour phase is known at given pressure. See Annex E for values of the distribution coefficient.

6.3 Injection

Either of the two following procedures can be used.

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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. Then inject the sample gas into the column by switching the passage of the 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. Measures should also 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, in volume %, of each component in sample gas according to Formula (1). Next, calculate the content, in mass %, of each composition to four decimal places according to Formula (2) in order to convert volume % to mass % and round off to three decimal places.

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

where

Cvi is the calculated concentration, in 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, in volume %, of compounds i in the last analysis of the WRM.

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

where

Cwi is the calculated concentration, in mass %, of compound i in the sample;

Mi is the molecular mass, in grams, of compounds i in the sample;

n is the 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.

8 Precision

The provisional precision of this method, established during interlaboratory tests relating to DME sample with components content shown below, and determined on the basis of statistical examination of interlaboratory test results is shown in Table 2. Refer to Annex D 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 2 — Provisional precision of the test method

Component	**Content in DME** mass %	**Repeatability** r mass %	**Reproducibility** R mass %
CO	0 to 0,010	0,46X	0,69X
CO$_2$	0 to 0,10	0,28X	0,28X
Methanol	0 to 0,050	0,16X	0,45X
Methyl formate	0 to 0,50	0,17X	0,41X
Ethyl methyl ether	0 to 0,20	0,50X	1,50X
Hydrocarbons up to C$_4$	0 to 0,050	0,14X	0,41X
NOTE X is the mean measured content value of each component.			

9 Test report

The test report shall include at least the following information:

a) a reference to this International Standard, i.e. ISO 17196:2014;

b) a reference to the gas chromatography system;

c) all the necessary information for complete identification of the sample, for example, ISO 29945:

— 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) a complete list of all components determined or detected;

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f) the details of any deviation from the procedure specified;

g) any unusual features noted during the determination (i.e. in the chromatogram).

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Annex A
(informative)

Examples of chromatographic systems and conditions (1)

A.1 Separation principles and procedures

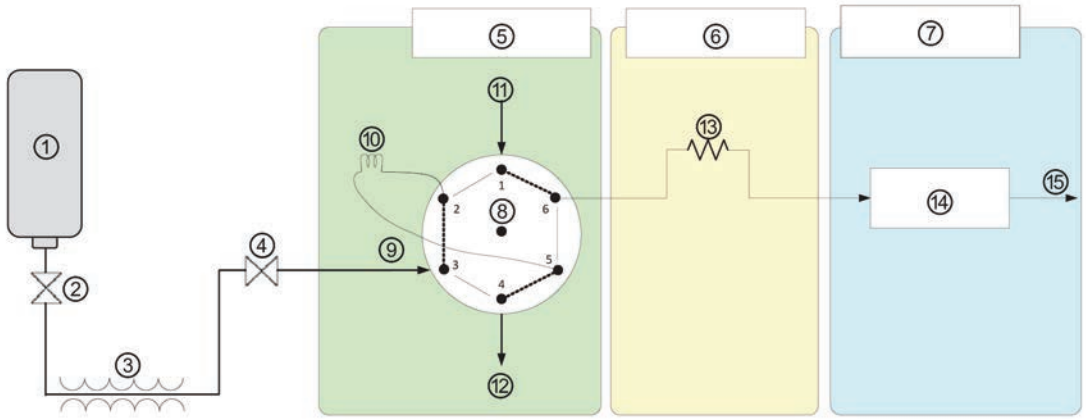
Analysis is performed separately by four injections on the gas chromatograph equipped with column, detector, and auto-gas sampler/injector system according to the following groups:

— CO_2 and hydrocarbons (up to C_4);

— methanol and methyl formate;

— ethyl methyl ether;

— CO.



Key

① sample cylinder
② mini valve
③ heater
④ control valve
⑤ injector
⑥ column oven
⑦ detector
⑧ valve
valve position off: – – – – – – –
valve position on: ————————
⑨ sample in
⑩ sample loop
⑪ carrier gas
⑫ sample out
⑬ column
⑭ TCD or FID
⑮ vent

Figure A.1 — Apparatus

Connect the bottom valve on the sample cylinder and the mini valve on the transfer line with short pipe (made of stainless steel with 3,18 mm of outer diameter and 1,74 mm of inner diameter, that is 0,72 mm of thickness). Heat the 650 mm portion of the transfer line tube to the temperature range within 80 °C~100 °C. This is achieved by heater attached to the tubing. Set the six-port sampling valve to the

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sampling position. Open the bottom valve and the mini valve. Using the flow adjuster valve, adjust the flow-rate of the sample gas to 0,5 l/min. Carry out the purging operation for at least 10 min to completely replace the remaining gas in the transfer line with the sample gas. After completion of enough purging operation mentioned above, turn the six-port sampling valve to the gas injection position. The sample is injected to the gas chromatograph and data collection is performed automatically.

A.2 Carbon dioxide and lower hydrocarbons

A.2.1 Column specification

- Column packing: VZ-7 (60/80mesh), 3 mm × 7,5 m (ID × length, stainless steel)
- Carrier gas flow rate: 20 ml/min of helium

A.2.2 Detection

- TCD
- Reference gas flow rate: 30 ml/min
- Detector temperature: 100 °C

A.2.3 Injection volume

- Air-actuated switching valves and 1,0 ml of gas sampler. It is an automatic gas injection by using auto-gas sampler with air actuated valves, which is controlled by an event timer.

A.2.4 Oven temperature

- Isothermal oven at 35 °C

A.2.5 Chromatogram example

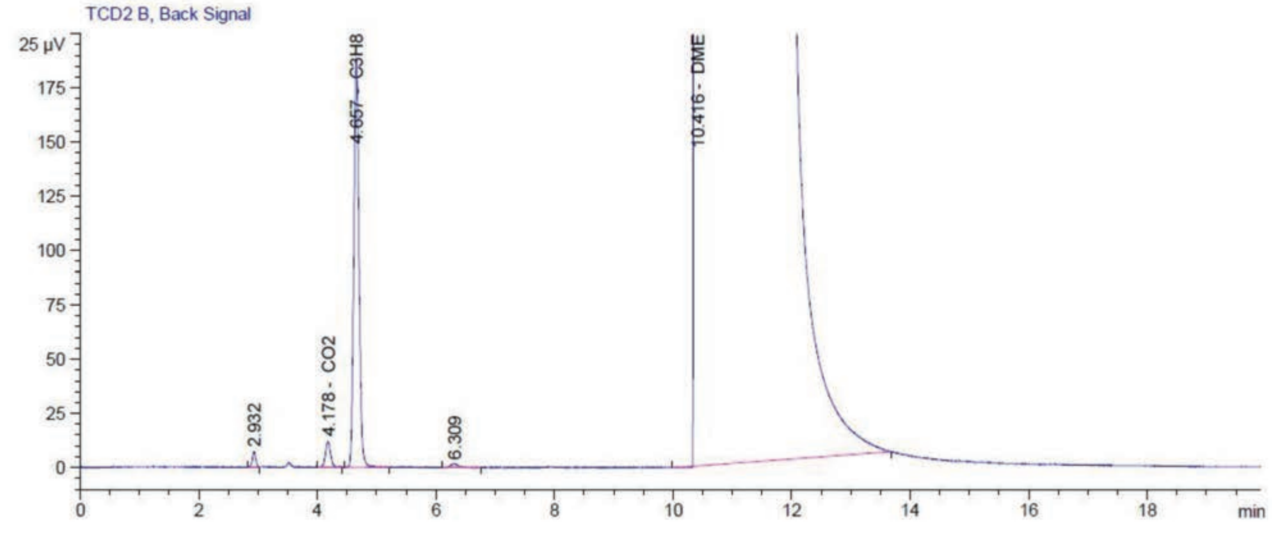


Figure A.2 — Chromatogram example

A.3 Methanol

A.3.1 Columns specification

- Column packing: PEG-20M 20 % chromosorb W (60/80 mesh) AW DMCS, 3 mm × 5 m (ID × length, stainless steel)
- Carrier gas flow rate: 20 ml/min of nitrogen

A.3.2 Detection

- FID, Detector temperature: 120 °C
- Hydrogen flow rate: 30 ml/min
- Air flow rate: 400 ml/min
- Make-up gas flow rate: 20 ml/min

A.3.3 Injection volume

- Air-actuated switching valve and 1 ml of gas sampler automatic gas injection by using auto-gas sampler with air-actuated valves, which is controlled by a timer

A.3.4 Oven temperature

- Isothermal oven at 90 °C

A.3.5 Chromatogram example

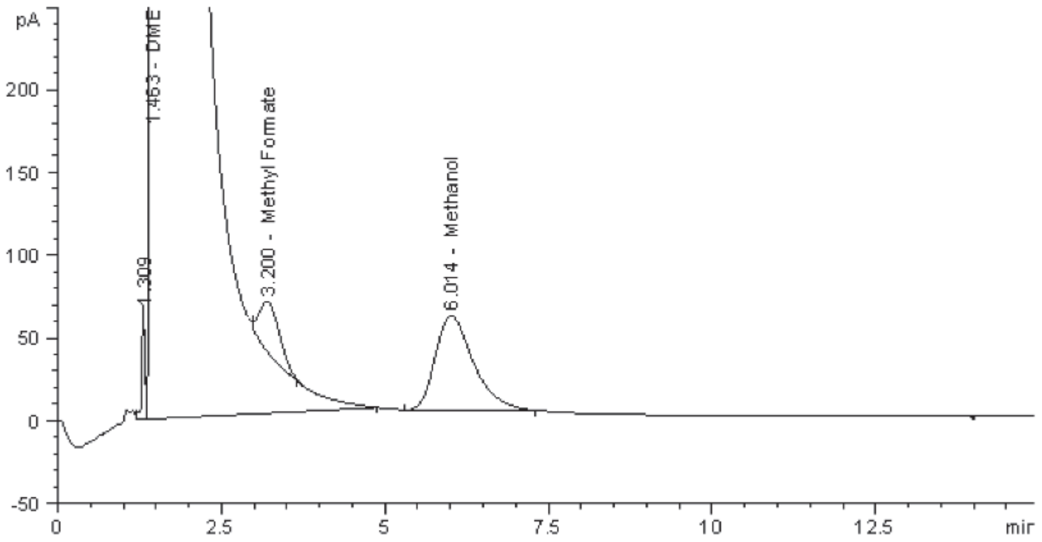


Figure A.3 — Chromatogram example

A.4 Methyl formate, ethyl methyl ether

A.4.1 Columns specification

- Column packing: Porapak T (60/80mesh), 3 mm × 2 m (ID × length, stainless steel)
- Carrier gas flow rate: 20 ml/min of nitrogen

A.4.2 Detection

- FID, detector temperature: 160 °C

— Hydrogen flow rate: 30 ml/min

— Air flow rate: 400 ml/min

— Make-up gas flow rate: 20 ml/min

A.4.3 Injection volume

— Air-actuated switching valve and 5 ml of gas sampler. It is an automatic gas injection by using auto-gas sampler with air-actuated valves, which is controlled by a timer.

A.4.4 Oven temperature

— Isothermal oven at 120 °C

A.4.5 Chromatogram example

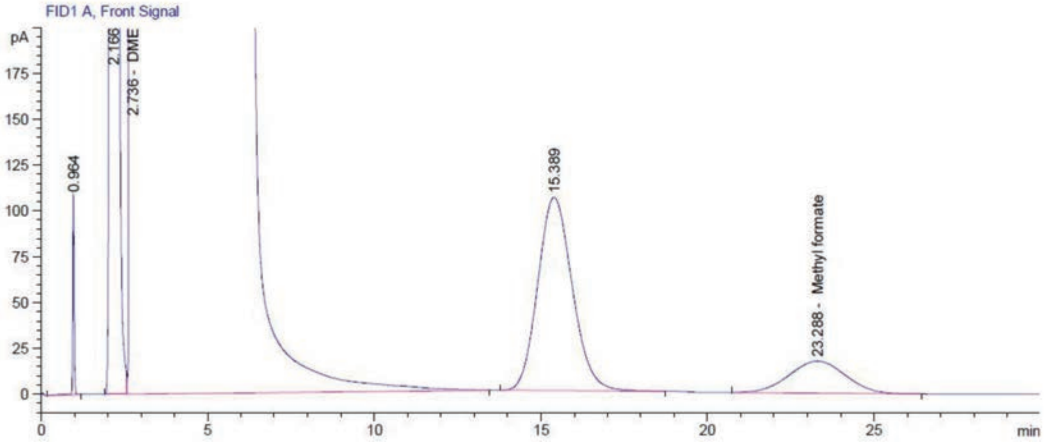
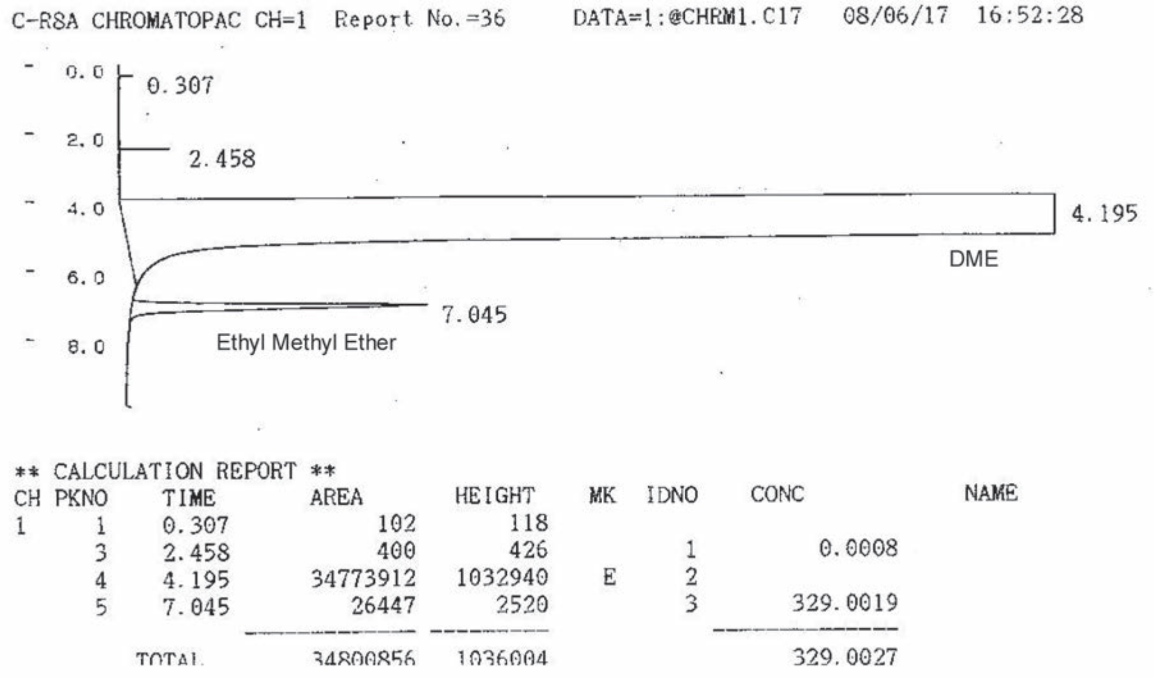


Figure A.4 — Chromatogram example



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C-R8A CHROMATOPAC CH=1  Report No.=36      DATA=1:@CHRM1.C17   08/06/17  16:52:28

** CALCULATION REPORT **
CH PKNO     TIME        AREA        HEIGHT     MK   IDNO    CONC              NAME
1     1     0.307          102         118
      3     2.458          400         426              1          0.0008
      4     4.195     34773912     1032940      E       2
      5     7.045        26447        2520              3        329.0019
                     ----------  ----------             -----------------
        TOTAL         34800856     1036004                       329.0027
```

Figure A.5 — Chromatogram example

A.5 Carbon monoxide

A.5.1 Columns specification:

- Column packing: Molecular sieve 5A (60/80mesh), 3 mm × 3 m (ID × length, stainless steel)
- Carrier gas flow rate: 20 ml/min of helium

A.5.2 Detection

- TCD, detector temperature: 130 °C
- Reference gas flow rate: 30 ml/min

A.5.3 Injection volume

- Air-actuated switching valve and 2 ml of gas sampler. It is an automatic gas injection by using auto-gas sampler with air actuated valves, which is controlled by timer.

A.5.4 Oven temperature

- Isothermal oven at 90 °C

A.5.5 Chromatogram example

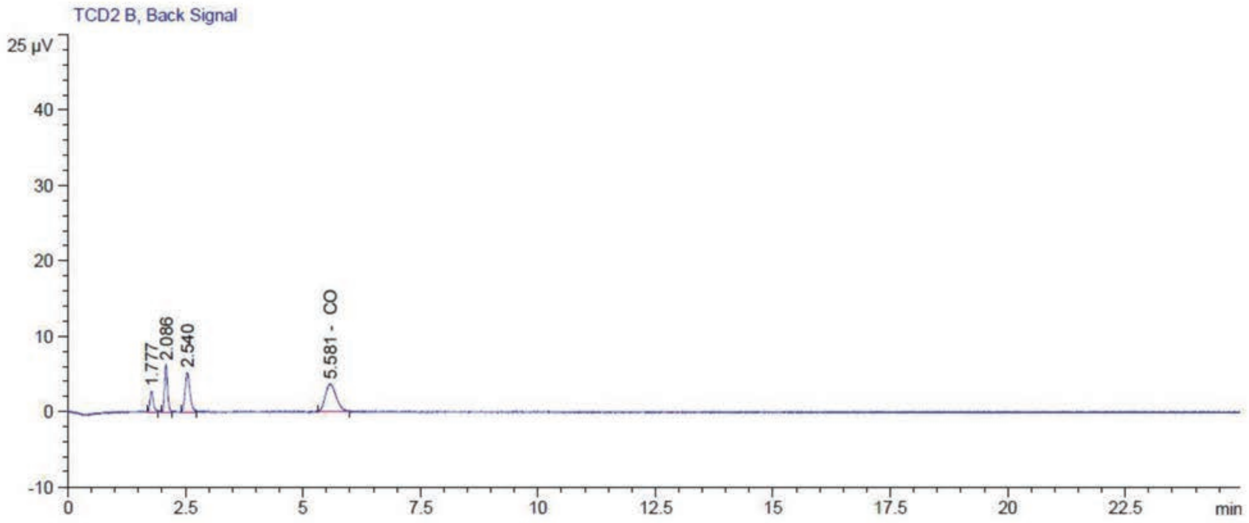


Figure A.6 — Chromatogram example

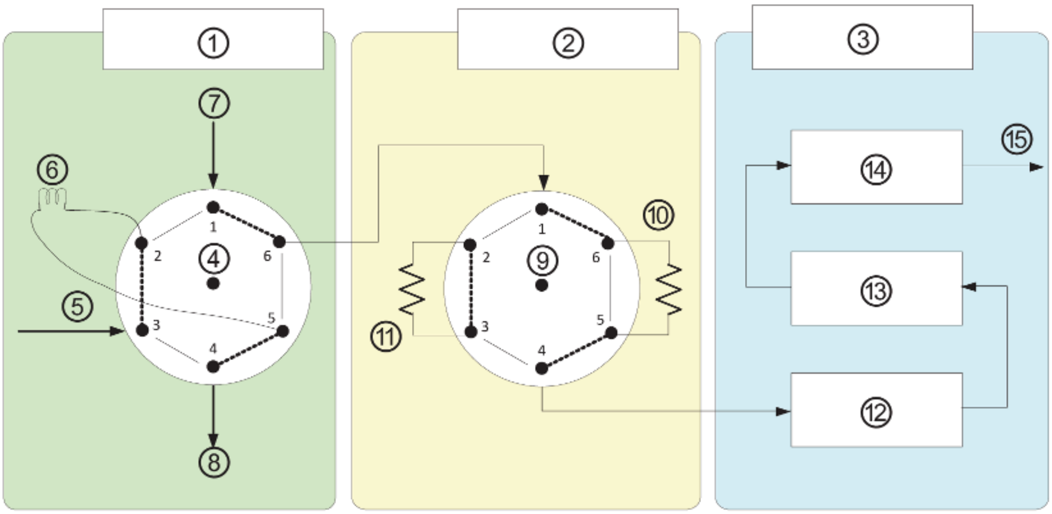
Annex B
(informative)

Examples of chromatographic systems and conditions (2)

B.1 Separation principles

This system contains two valves: one is for sample injection and the other is for switching two columns. Valve #1 (GSV1) is for loading the sample. The valve is located on the sampling loop. The sample is loaded with the valve in the off-position, and turned to the on-position when the sample is ready to be injected into the GC system. Valve #2 (GSV2) is a switching valve. When turned to the off-position, the sample is passed through both columns, while, when it is in the on-position, the sample is passed only through the Porapak N column.

The Methanizer enables the flame ionization detector (FID) to detect low levels of CO which are not ionized by the flame, by methanizing the samples with the Ni-Catalyst.



Key

①	injector
②	column oven
③	detector
④	valve 1
⑤	sample in
⑥	sample loop
⑦	carrier gas
⑧	sample out
⑨	valve 2
⑩	column 1
⑪	column 2
⑫	TCD
⑬	methanizer
⑭	FID
⑮	vent

Figure B.1 — Apparatus

B.2 Column specification

1) Name: Porapak Q/Porapak N

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2) Mesh: 80/100 mesh

3) Length: 18 ft

4) Diameter: 1/8 in

5) Pipe material: Stainless steel

6) Carrier gas

   — TCD: Argon, 30 ml/min; FID: Argon, 20 ml/min

B.3 Detection

A TCD and an FID are used as the detectors. The TCD is maintained at a temperature of 200 °C, and the FID is ignited in a condition where the hydrogen supply flow rate is 30 ml/min and the air supply flow rate is 300 ml/min, and is maintained at a temperature of 250 °C.

Its sensitivity shall be sufficient enough to generate a minimum of 0,5 mV signal for 1 mol % methane (CH_4) component in 0,25 ml of sample volume.

B.4 Injection volume

Sample injection volume is 250 µl sample loop in injector.

B.5 Oven temperature

Temperature zone is maintained at a temperature of 40 °C during 2 min and rising rate is 10 ° C/min to 120 °C and maintained at a temperature of 120 °C during 20 min.

B.6 Chromatogram examples

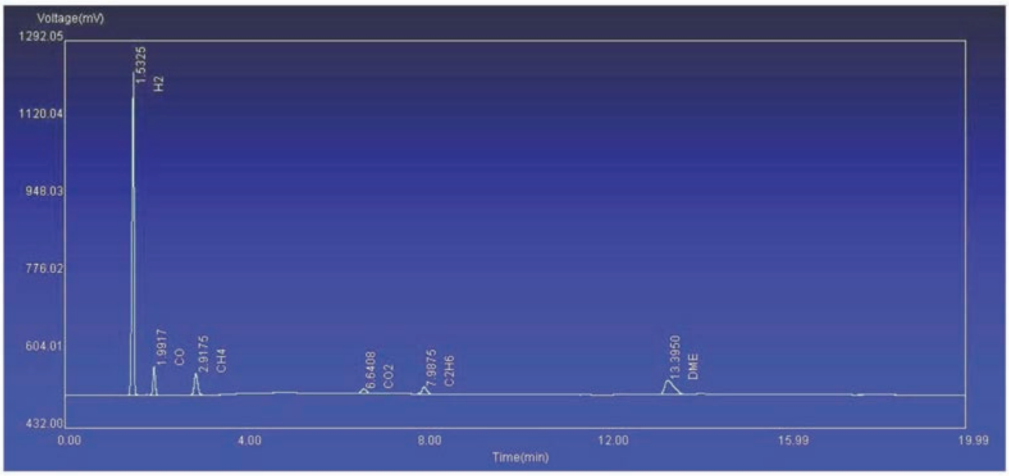

Figure B.2 — Analysis result example of reference standard gas (TCD detector)

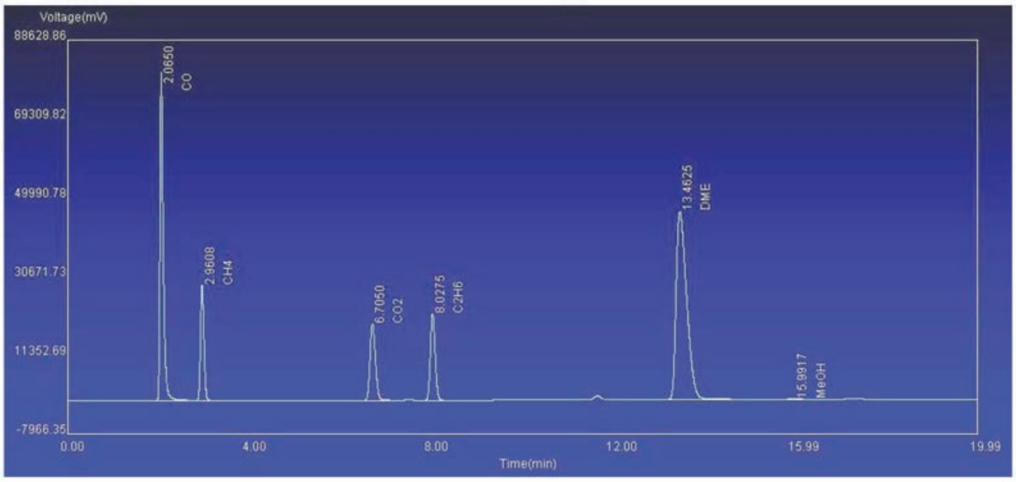

Figure B.3 — Analysis result example of reference standard gas (FID detector)

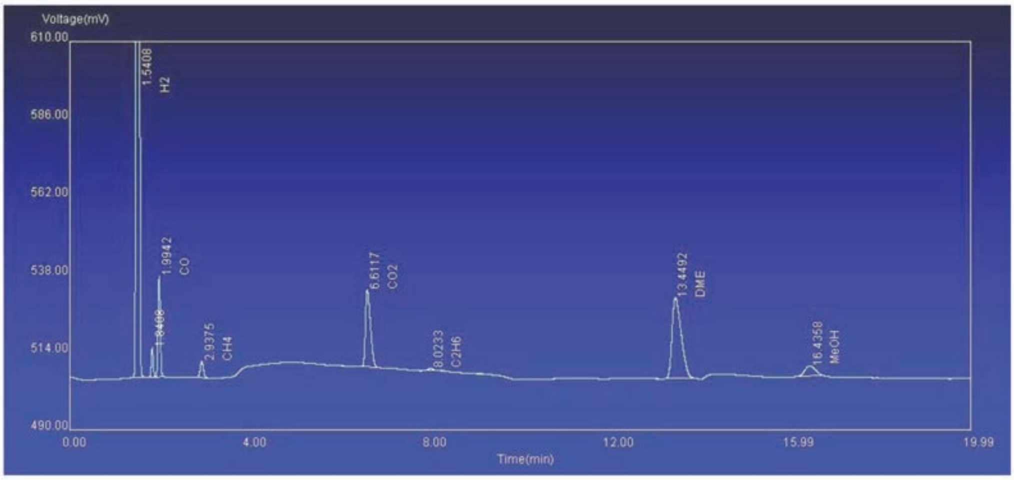

Figure B.4 — Analysis result example (TCD detector)

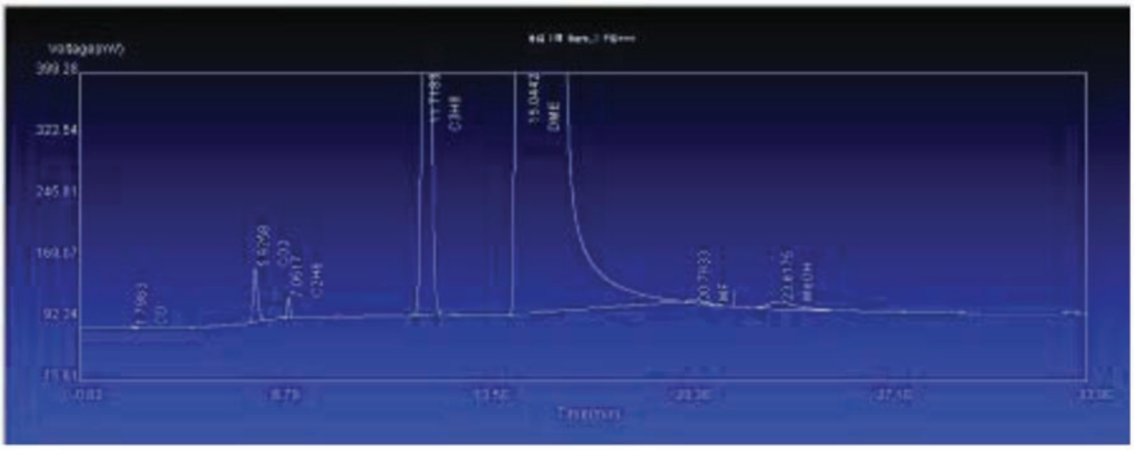

Figure B.5 — Analysis result example (FID detector)

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Annex C
(informative)

Example of working reference gas mixture

C.1 General

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 specifications of ISO 16861.

C.2 Example of WRM

NOTE WRM gas mixtures can be prepared by gravimetric method in accordance with ISO 6142 or certified and validated by comparison with gas mixtures in accordance with ISO 6143. It can also be purchased from reliable commercial vendors.

Examples of WRM is shown in Table C.1 to C.5.

Table C.1 — Example of WRM for hydrocarbons up to C_4

Component	**Concentration** volume %
Ethane	0,025 4
Ethylene	0,025 4
Propane	0,025 7
Propylene	0,025 8
n-butane	0,025 6
i-butane	0,025 8
1-butene	0,025 3
i-butene	0,024 8
cis-2-butene	0,026 1
trans-2-butene	0,025 4
Helium	Balance

Table C.2 — Example of WRM for CO and CO_2

Component	**Concentration** volume %
CO	0,005 3
CO_2	0,054 5
Helium	Balance

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Table C.3 — Example of WRM for methanol

Component	**Concentration** volume %
Methanol	0,025 0
N_2	Balance

Table C.4 — Example of WRM for methyl formate

Component	**Concentration** volume %
Methyl formate	0,023 9
N_2	Balance

Table C.5 — Example of WRM for ethyl methyl ether

Component	**Concentration** volume %
Ethyl methyl ether	0,103 0
N_2	Balance

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Annex D
(informative)

Report of the interlaboratory tests

D.1 Precision

a) 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 five or six laboratories.

b) Interlaboratory test results

The precisions were 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 of CO are shown in Table D.1. These values were determined from a level experiment involving five laboratories with 0,001 3 mass % of sample, in which one statistical outlier was detected by Cochran's test and retained.

Table D.1 — Interlaboratory test results (CO)

Dimensions in mass %

Laboratory	**1st**	**2nd**	**3rd**	**4th**	**5th**	**Average**	**Standard deviation**	**Number of tests**
L1	0,001 52	0,001 64	–	–	–	0,001 58	0,000 09	2
L2	0,000 80	0,000 98	0,000 78	0,001 20	0,000 76	0,000 90	0,000 19	5
L3	0,002 5	0,003 6	0,001 1	–	–	0,002 4	0,001 3	3
L4	0,001	0,002	0,002	–	–	0,002	0,001	3
L5	0,000 44	0,000 50	0,000 44	0,000 63	–	0,000 50	0,000 09	4
The general mean	0,001 3							
All number of tests	17							
Repeatability standard deviation	0,000 6							
Reproducibility standard deviation	0,000 9							

The test results of CO_2 are shown in Table D.2. These values were determined from a level experiment involving six laboratories with 0,006 4 mass % of sample, in which one statistical outlier was detected by Cochran's test and one straggler was detected by Grubbs' test and retained.

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Table D.2 — Interlaboratory test results (CO_2)

Dimensions in mass %

Laboratory	1st	2nd	3rd	4th	5th	Average	Standard deviation	Number of tests
L1	0,006 31	0,007 37	–	–	–	0,006 84	0,000 74	2
L2	0,006 32	0,006 37	0,006 06	0,006 54	0,006 26	0,006 31	0,000 17	5
L3	0,010 0	0,001 5	0,004 6	–	–	0,005 4	0,004 3	3
L4	0,007 7	0,005 7	0,006 4	–	–	0,006 6	0,001 0	3
L5	0,008	0,006	0,006	–	–	0,007	0,001	3
L6	0,006 31	0,007 25	0,006 53	0,006 95	–	0,006 76	0,000 42	4
The general mean	0,006 4							
All number of tests	20							
Repeatability standard deviation	0,001 8							
Reproducibility standard deviation	0,001 8							

The test results of methanol are shown in Table D.3. These values were determined from a level experiment involving six laboratories with 0,016 0 mass % of sample, in which one straggler was detected by Cochran's test and retained.

Table D.3 — Interlaboratory test results (Methanol)

Dimensions in mass %

Laboratory	1st	2nd	3rd	4th	5th	Average	Standard deviation	Number of tests
L1	0,018 7	0,018 9	–	–	–	0,018 8	0,000 1	2
L2	0,015 25	0,016 36	0,017 43	0,016 59	0,016 65	0,016 46	0,000 79	5
L3	0,022 0	0,015 7	0,010 9	–	–	0,016 2	0,005 6	3
L4	0,028 5	0,024 2	0,031 4	–	–	0,028 0	0,003 6	3
L5	0,015	0,016	0,014	–	–	0,015	0,001	3
L6	0,008 83	0,007 21	0,007 33	0,007 18	0,007 45	0,007 60	0,000 70	5
The general mean	0,016 0							
All number of tests	21							
Repeatability standard deviation	0,002 5							
Reproducibility standard deviation	0,007 2							

The test results of methyl formate are shown in Table D.4. These values were determined from a level experiment involving six laboratories with 0,008 8 mass % of sample, in which one statistical outlier was detected by Cochran's test and retained.

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Table D.4 — Interlaboratory test results (Methyl formate)

Dimensions in mass %

Laboratory	1st	2nd	3rd	4th	5th	Average	Standard deviation	Number of tests
L1	0,006 1	–	–	–	–	0,006 1	–	1
L2	0,008 87	0,009 07	0,009 50	0,009 06	0,009 22	0,009 14	0,000 24	5
L3	0,011 2	0,011 1	0,010 6	–	–	0,011 0	0,000 3	3
L4	0,010 2	0,009 1	0,010 7	–	–	0,010 0	0,000 8	3
L5	0,010	0,012	0,017	–	–	0,013	0,004	3
L6	0,004 72	0,005 49	0,003 64	0,003 21	0,004 46	0,004 30	0,000 90	5
The general mean	0,008 8							
All number of tests	20							
Repeatability standard deviation	0,001 5							
Reproducibility standard deviation	0,003 6							

The test results of HC (up to C_4) are shown in Table D.5. These values were determined from a level experiment involving six laboratories with 0,095 2 mass % of sample, in which one statistical outlier was detected by Cochran's test and Grubbs' test, respectively, and retained.

Table D.5 — Interlaboratory test results [HC (up to C_4)]

Dimensions in mass %

Laboratory	1st	2nd	3rd	4th	5th	Average	Standard deviation	Number of tests
L1	0,039 38	0,023 89	0,024 78	0,023 89	–	0,027 99	0,007 61	4
L2	0,104 25	0,103 40	–	–	–	0,103 82	0,000 60	2
L3	0,119 6	0,155 1	0,097 1	–	–	0,123 9	0,029 2	3
L4	0,110 5	0,105 6	0,108 9	–	–	0,108 3	0,002 5	3
L5	0,101 7	0,122 7	0,100 7	–	–	0,108 4	0,012 4	3
L6	0,107 79	0,103 00	0,113 72	0,126 87	0,110 80	0,112 43	0,008 99	5
The general mean	0,095 2							
All number of tests	20							
Repeatability standard deviation	0,013 4							
Reproducibility standard deviation	0,039 3							

The test results of ethyl methyl ether are shown in Table D.6. These values were determined from a level experiment involving five laboratories with 0,000 2 mass % of sample, in which one straggler was detected by Cochran's test and retained.

Table D.6 — Interlaboratory test results (Ethyl methyl ether)

Dimensions in mass %

Laboratory	1st	2nd	3rd	4th	5th	Average	Standard deviation	Number of tests
L1	0,000 00	0,000 00	0,000 00	0,000 00	0,000 00	0,000 00	0,000 00	5
L2	0,000 00	0,000 0	0,000 0	–	–	0,000 00	0,000 00	3
L3	0,000 3	0,000 2	0,000 2	–	–	0,000 2	0,000 2	3
L4	0,000 8	0,000 6	0,000 5	–	–	0,000 6	0,000 2	3
L5	0,000 0	0,000 00	0,000 00	–	–	0,000 0	0,000 0	3
The general mean	0,000 2							
All number of tests	17							
Repeatability standard deviation	0,000 1							
Reproducibility standard deviation	0,000 3							

c) 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 interlaboratory test because of limited samples and time. Therefore, the tolerance of the 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 the repeatability and the reproducibility standard deviation is shown in Figure D.1.

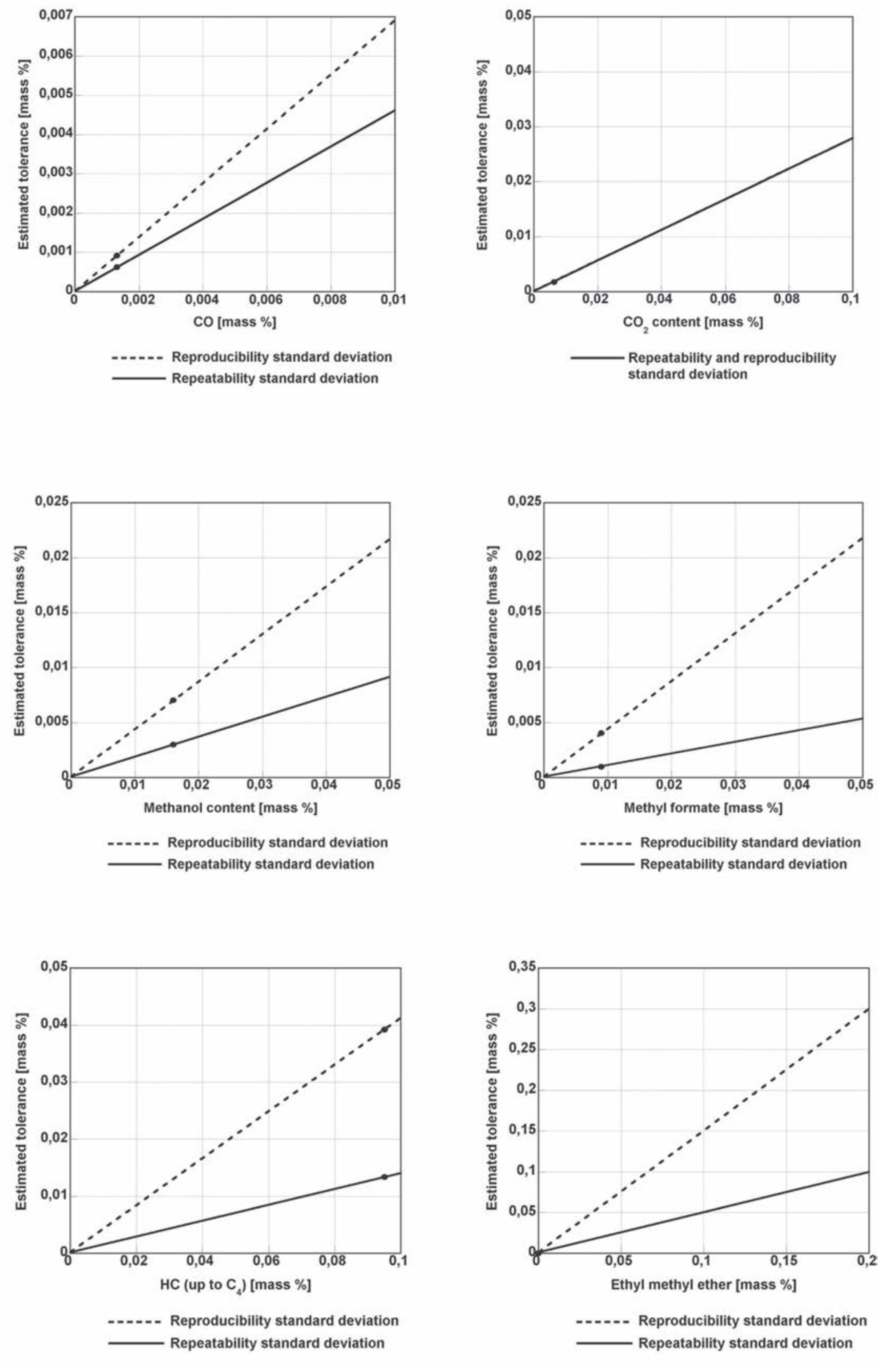

Figure D.1 — Estimated tolerance of the repeatability and the reproducibility standard deviation

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Annex E

(informative)

Solubility of CO and CO_2 in DME

E.1 Solubility of CO and CO_2 in DME

E.1.1 Effect of CO partial pressure on solubility of CO in DME

Effect of CO partial pressure on solubility of CO in DME was measured by gas chromatography (GC). CO was injected into a cylinder in which liquid pure DME was filled with various pressures. After injection of CO, the cylinder was shuffled to blend CO and DME as a test sample. The sample was introduced to GC by liquid from the bottom of the sample cylinder, then, CO concentration in DME was measured by GC.

Test conditions:

- Sample: pure DME + CO;
- Room temperature: 18,7 °C.

Test results:

The test results of CO concentration in DME are shown in Table E.1 and Figure E.1. CO concentrations in DME were increasing with rising of CO partial pressure. If CO concentration is set at 0,01 mass %, 0,0194 MPa of the CO partial pressure is necessary.

Table E.1 — Test results of CO concentration in DME

No.	**Pressure** MPaG	**Partial pressure (CO)** MPa	**CO concentration** mass %			
			***n* = 1**	***n* = 2**	***n* = 3**	**Ave.**
0	0,4	0,0	0	0	0	0
1	0,5	0,1	0,248	0,202	0,182	0,211
2	1,0	0,6	0,569	0,526	0,529	0,541
3	1,5	1,1	1,033	0,912	0,954	0,966
4	2,0	1,6	1,233	1,611	1,416	1,420
5	2,5	2,1	2,556	2,5706	2,589	2,572

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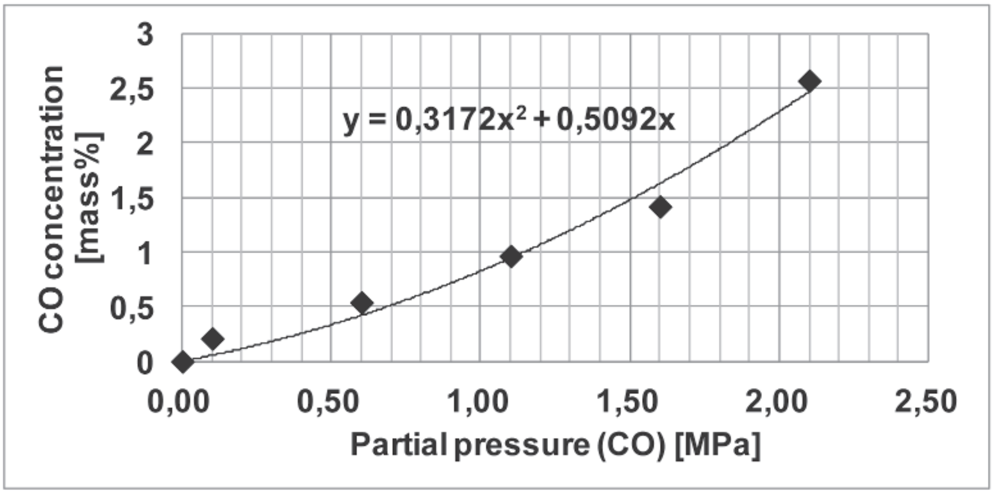

Figure E.1 — Test results of CO concentration in DME

E.1.2 Effect of CO_2 partial pressure on solubility of CO_2 in DME

Effect of CO_2 partial pressure on solubility of CO_2 in DME was measured by GC. Gas state of CO_2 was injected into a cylinder in which liquid pure DME was filled with various pressures. After injection of CO_2, the cylinder was shuffled to blend CO_2 and DME as a test sample. The sample was introduced to GC by liquid from the bottom of the sample cylinder, then, CO_2 concentration in DME was measured by GC.

Test conditions:

- Sample: pure DME + CO_2;
- Room temperature: 18,5 °C.

Test results:

The test results of CO_2 concentration in DME are shown in Table E.2 and Figure E.2. CO_2 concentrations in DME were increasing with rising of CO_2 partial pressure. If CO_2 concentration is set at 0,1 mass %, 0,0825 MPa of the CO_2 partial pressure is necessary.

Table E.2 — Test results of CO_2 concentration in DME

No.	Pressure MPaG	Partial pressure (CO) MPa	CO concentration mass %			
			n = 1	*n* = 2	*n* = 3	Ave.
0	0,4	0,0	0	0	0	0
1	0,5	0,1	0,263	0,271	0,278	0,271
2	1,0	0,6	1,109	1,088	1,134	1,111
3	1,5	1,1	2,445	2,500	2,471	2,472
4	2,0	1,6	1,233	1,611	1,416	1,420
5	2,5	2,1	2,556	2,570	2,589	2,572

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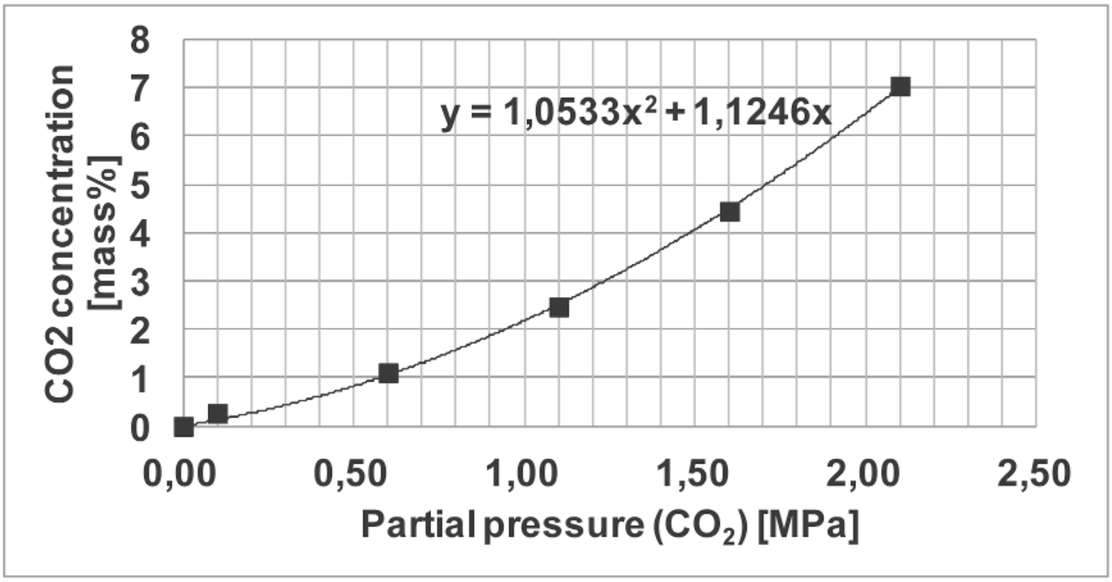

Figure E.2 — Test results of CO_2 concentration in DME

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Bibliography

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

[2] ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method*

[3] ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

[4] ISO 7504, *Gas analysis — Vocabulary*

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