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Edition 1.0 2021-07

TECHNICAL REPORT

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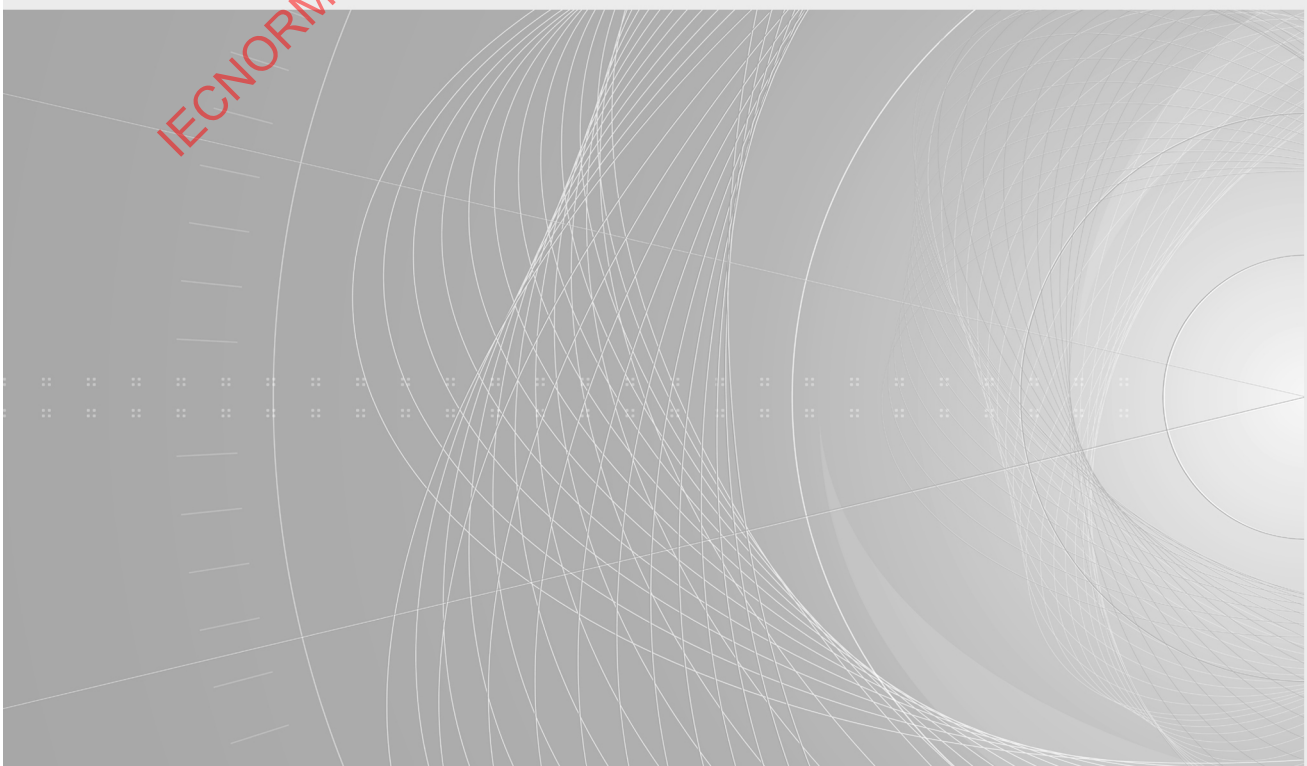
Insulating liquids – Quantitative determination of methanol and ethanol in insulating liquids



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INTERNATIONAL
ELECTROTECHNICAL
COMMISSION

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CONTENTS

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INSULATING LIQUIDS – QUANTITATIVE DETERMINATION OF METHANOL AND ETHANOL IN INSULATING LIQUIDS

FOREWORD

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IEC TR 63025 has been prepared by IEC technical committee 10: Fluids for electrotechnical applications. It is a Technical Report.

The text of this Technical Report is based on the following documents:

Draft	Report on voting
10/1112/DTR	10/1131/RVDTR

Full information on the voting for its approval can be found in the report on voting indicated in the above table.

The language used for the development of this Technical Report is English.

This document was drafted in accordance with ISO/IEC Directives, Part 2, and developed in accordance with ISO/IEC Directives, Part 1 and ISO/IEC Directives, IEC Supplement, available at www.iec.ch/members_experts/refdocs. The main document types developed by IEC are described in greater detail at www.iec.ch/standardsdev/publications.

The committee has decided that the contents of this document will remain unchanged until the stability date indicated on the IEC website under webstore.iec.ch in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

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INTRODUCTION

It has been demonstrated over several years that the ageing of impregnated paper in insulating liquid, which results in cellulose degradation, produces molecules of light alcohols, methanol (MeOH) and ethanol (EtOH). In laboratory experiments, a good correlation has been established between the increase of the methanol content in insulating liquid and the decrease of the degree of polymerization of the cellulose, irrespective of the type of paper, standard kraft or thermally upgraded. Further, at the early stages of paper ageing, i.e. of cellulose degradation, the methanol content is always higher than that of furanic compounds (mainly 2-furfural), so this behaviour suggests that methanol could be a relevant in-oil marker to detect early paper ageing in transformers and to assess its evolution (see Figure 1).

Ethanol is a second light alcohol of interest that these methods would be able to detect.

It should be emphasized that in a real transformer the situation is much more complicated than in laboratory setups, so the relationship between in situ paper degradation and tracer concentration (MeOH, EtOH, as well as 2-FAL) is much more complex and hard to establish.

In order to address the growing interest of industry in using these alcohols as tracers of cellulosic material ageing in operating equipment, there is a need for the development of a document describing analytical methods to quantify methanol and ethanol in the different types of insulating liquids. The objective is for one of these methods to remain as simple and affordable as possible, and for the other to be more sophisticated and more accurate.

The principle of this Technical Report was brought up and discussed during the IEC TC 10 plenary meeting held in Vienna in November 2013. A project team was set up to prepare test methods for the unambiguous quantitative determination of methanol and ethanol in unused and used insulating liquids.

WARNING – Health and safety

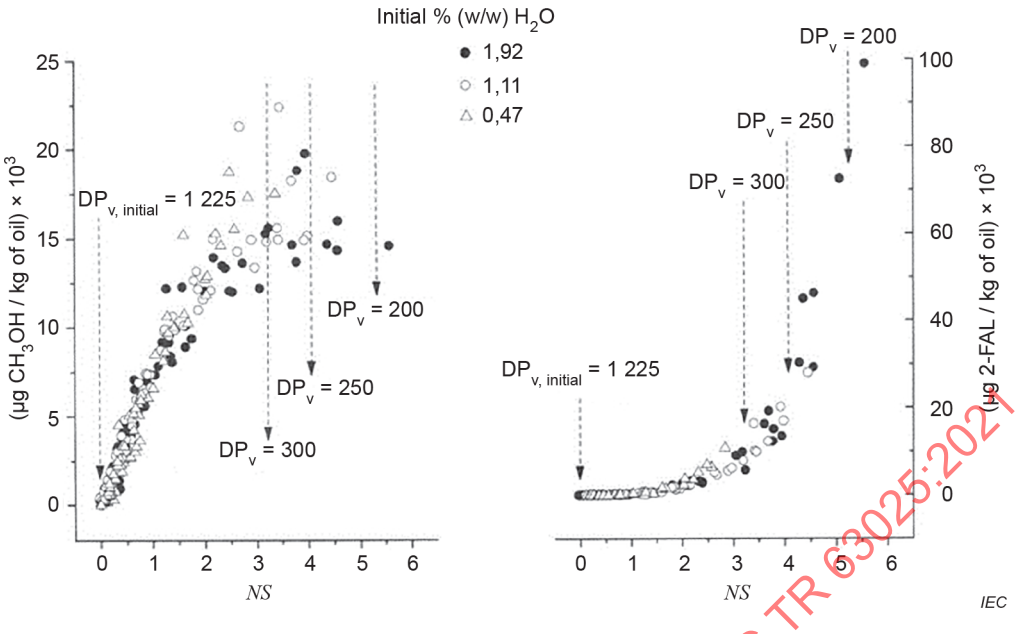
This document does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

The insulating liquids which are the subject of this document should be handled with due regard to personal hygiene. Direct contact with eyes may cause slight irritation. In the case of eye contact, irrigation with copious quantities of clean running water should be carried out and medical advice sought.

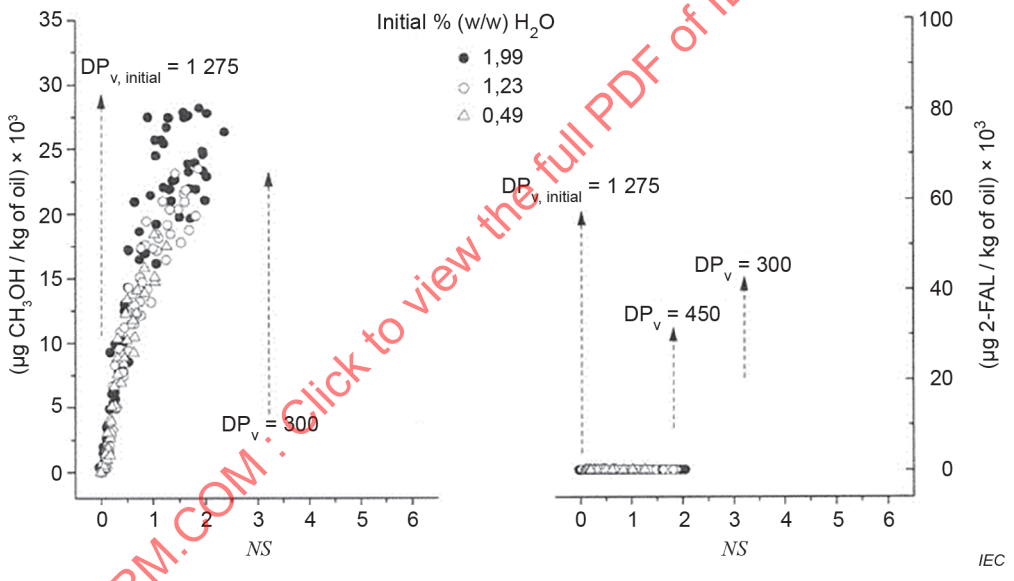
Some of the tests specified in this document involve the use of processes that could lead to a hazardous situation. Attention is drawn to the relevant standard for guidance.

WARNING – Environment

This document involves mineral oils, ester liquids, chemicals and used sample containers. The disposal of these items should be carried out in accordance with current national legislation with regard to their impacts on the environment. Every precaution should be taken to prevent the release into the environment of the chemicals used during the test.



a) Clupak HD75 specimens



b) Manning 220 mannitherm D specimens

Key

NS: number of scissions, inversely proportional to the polymerization degree (DPv)

a): standard kraft paper

b): thermally upgraded paper

NOTE See Jalbert J., Gilbert R., Tétreault P., Morin B. and Lessard-Déziel D. (2007) in the Bibliography.

Figure 1 – Comparison of methanol and 2-furfural production in mineral oil versus cellulose scission number

INSULATING LIQUIDS – QUANTITATIVE DETERMINATION OF METHANOL AND ETHANOL IN INSULATING LIQUIDS

1 Scope

This document specifies two test methods for methanol and ethanol determination in insulating liquids.

Methanol (MeOH) and ethanol (EtOH) are two light alcohols generated during the degradation process of cellulosic materials. They are soluble in insulating liquids so they can be regarded as ageing tracers whose concentrations in oil reflect the degradation of insulating cellulosic materials in liquid-impregnated transformers.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1
flame ionization detector
device in which hydrocarbons are burned in a hydrogen-air flame and the electrical current caused by the resulting ions is measured between two electrodes

Note 1 to entry: The flame ionization detector is used in gas chromatography mainly to detect hydrocarbon compounds.

[SOURCE: ISO 14532:2014, 2.4.8, modified – "detector" replaced with "device".]

3.2
gas chromatograph
GC
device used to determine complex mixture components that can be vaporized without decomposition then separated by differential migration with a carrier gas through a stationary phase in a column

Note 1 to entry: The method used is called "gas chromatography" (GC).

[SOURCE: IEC 62697-1:2012, 3.1.14, modified – "used for separating volatile and semi-volatile compounds in mixtures" replaced with "used to determine complex mixture components", "through differential migration" replaced with "then separated by differential migration" and "a stationary phase" and Note 1 to entry added.]

3.3
headspace extraction
procedure for collecting the volatile compounds emitted by a specimen enclosed in an airtight vial under controlled conditions

Note 1 to entry: The gaseous phase is assumed to contain the volatile compounds in equilibrium with that present in the specimen in the vial (via Henry's partition coefficient).

[SOURCE: ISO 8873-3:2007, 3.7, modified – In the term "analysis" replaced with "extraction", definition revised and note replaced with the Note to entry.]

3.4
internal standard
IS
compound, different from target analytes but as similar as possible in its properties (structure, polarity, etc.) and analytical response, which is added in the tested sample in a known amount and detected simultaneously with the analytes

Note 1 to entry: A defined volume of the internal standard solution is added to both the sample and calibration solution such that they both contain an identical concentration.

[SOURCE: IEC 62697-1:2012, 3.1.12, modified – Definition revised.]

3.5
mass spectrometer
MS
instrument used for ionizing neutral chemical species, separating ions according to their mass to charge ratio (m/z) and then detecting selected ions

Note 1 to entry: It permits determining concentrations of target analytes in complex mixtures such as insulating liquids.

Note 2 to entry: The method used is called "mass spectrometry" (MS).

[SOURCE: IEC 62697-1:2012, 3.1.15, modified – "(m/z) and then detecting selected ions" added, in the Note 1 to entry "compounds" replaced with "analytes" and Note 2 to entry added.]

4 Symbols and abbreviated terms

For the purposes of this document, the following symbols and abbreviated terms are used.

DMSO	dimethyl sulfoxid
EtOH	ethanol (CH_3-CH_2-OH)
FID	flame ionization detector
GC	gas chromatography / gas chromatograph
HS	headspace (vial/extraction/sampler)
HS-CG-MS	gas chromatograph, with headspace sampler, coupled with a mass spectrometer detector (Method A)
HS-CG-FID	gas chromatograph, with headspace sampler, coupled with a flame ionization detector (Method B)
IS	internal standard
MeOH	methanol (CH_3-OH)
MS	mass spectrometer (detector)
PLOT	porous layer open tubular
PTFE	polytetrafluoroethylene
RT	retention time
RF	response factor
SIM	selected-ion monitoring
TIC	total ion current
TOGA	total oil gas analysis

5 Sampling

Insulating liquid is sampled in a glass syringe following the procedure given in IEC 60475:2011, 4.2.2 that provides guidance for the sampling of insulating liquids for dissolved gas analysis.

A representative sample requires a sufficient purge of the injection system of the apparatus, to ensure that the stagnant insulating liquid in the valve is eliminated.

NOTE Sampling is preferably performed in a glass syringe or suitable aluminium can or glass bottle filled to the top according to DGA sampling practices specified in IEC 60475:2011, 4.2.1.5.

6 Principle of the methods

The analysis requires extraction of MeOH and EtOH from an insulating liquid sample in a closed vial with free space, and then injection of the gaseous phase into a chromatograph. MeOH and EtOH are separated from the other volatile constituents of the sample through a suitable capillary column, and detected at the outlet of the column using a mass spectrometer or a flame ionization detector.

Their quantification is done using external calibration curves or by the internal standard technique.

The two elected methods are:

- Method A: gas chromatography with headspace sampler, coupled with a mass spectrometer detector (HS-GC-MS), and
- Method B: gas chromatography with headspace sampler, coupled with a flame ionization detector (HS-GC-FID):

The MeOH quantification limit is around 10 µg · kg^{-1} with both methods.

NOTE Method B can be less sensitive in the case of heavily aged liquids.

7 Method A – HS-GC-MS

7.1 General

Differences between gas chromatographs, headspace samplers and mass spectrometer detectors from different manufacturers make it impractical to specify detailed operating conditions. Refer to the manufacturer's instructions for instrument setup to allow optimized separation and detection of MeOH and EtOH.

7.2 Apparatus

7.2.1 Analytical balance

A balance with a precision at 4^{th} gram decimal (0,000 1 g) or better is used.

7.2.2 Headspace sampler

HS sampler equipped with an oven capable of heating the HS vials up to 90 °C, running with mechanical shaking. Its injection loop and transfer line are connected to the injection port of the gas chromatograph.

Injection volume is in the range of 250 µl to 1 000 µl.

7.2.3 Gas chromatograph coupled with mass spectrometry detector

A gas chromatograph equipped with a mass spectrometry detector is used.

A split/splitless injector can be used but other injection techniques are suitable (e.g. on-column).

The use of a porous layer open tubular (PLOT) GC column is preferred to achieve adequate peak separation and to achieve good detection limits. A capillary column for light alcohols, 10 m to 60 m long, low bleeding, giving the appropriate separation of the analytes and potential interferents is opted for.

NOTE 624-type capillary columns were found suitable for the purpose. Other columns can be used if appropriate peak separation is obtained.

A single quadrupole MS detector is sufficient to obtain the required quantification limit, however devices which demonstrate similar or better quantification limits can also be used (e.g. high resolution mass spectrometer, tandem mass spectrometer, ion trap).

7.3 Reagents and materials

7.3.1 Laboratory equipment and glassware

The vessels and accessories used for the tests are cleaned and prepared with analytical grade solvents.

NOTE 1 To ensure that all glassware and accessories are free from MeOH and EtOH, they can be heated in an oven at 100 °C for 1 h to 2 h and brought back to room temperature prior to their use.

- headspace glass vials of 20 ml nominal capacity, with crimp- or screw-type caps and polytetrafluoroethylene (PTFE) faced butyl septa;

NOTE 2 Vials and septa fulfilling the IEC 60567 requirements are suitable.

NOTE 3 Other volumes of vials are suitable (e.g. 10 ml).

- crimping system;
- Class A volumetric flasks;
- standard flask with stopper, in a precision class with a tolerance of ≤ 0,1 %;
- volumetric dispensers in a precision class compatible with the required uncertainty of measure; volumetric dispensers with a precision of ±1 % can be accepted;
- certified amber glass vials of 2 ml with screw neck ND10 and certified suitable caps in PTFE/white silicone;
- glass syringes, gas tight, 20 ml to 50 ml equipped with three-way glass (stainless steel) or PTFE stopcocks for dosing the insulating liquid during calibration and analysis;
- micro-syringes for gas chromatography of suitable volume (usually 10 µl);
- glass balls of 2 mm diameter for easier solution homogenization.

7.3.2 Standard chemicals

- unused insulating liquid that is free from MeOH and EtOH. To remove eventual residues of MeOH and EtOH, see 7.4.2;
  - mineral oil conforming to IEC 60296 specifications;
  - synthetic esters conforming to IEC 61099 specifications;
  - natural esters conforming to IEC 62770 specifications;
- methanol (CH_4O), analytical grade, anhydrous (purity > 99 %);
- ethanol (C_2H_6O), analytical grade, anhydrous (purity > 99 %);
- deuterated ethanol (C_2D_6O) as internal standards (deuterium, D or ^2H);

- dimethyl sulfoxid, DMSO (C_2H_6OS), HS-GC tested ≥ 99,9 %.

NOTE 1 Other internal standards, such as deuterated methanol (CD_4O), ^{13}C-methanol ($^{13}CH_4O$) or ^{13}C-ethanol ($^{13}C_2H_6O$), can be used if validated.

NOTE 2 Deuterated molecules are less stable than ^{13}C-alcohols because of readily hydrogen-deuterium exchanges in the hydroxyl group (-OH).

7.3.3 GC carrier gases

- Helium (He) purity 6.0 (99,999 9 %).

7.4 Preparation of standard solutions

7.4.1 General

The insulating liquid used to prepare the standard solutions are of the same type (mineral oil, ester,etc.) as the samples to be tested.

7.4.2 Degassed insulating liquid

A suitable volume of unused insulating liquid is degassed under vaccum (≤ 1 Pa) for 24 h, to remove traces of methanol and ethanol present.

The objective is for the final liquid to have contents of methanol and ethanol below 10 µg · kg^{-1}.

NOTE This step can be avoided if the unused insulating liquid can be proven to have MeOH and EtOH contents three times lower than the required quantification limits.

7.4.3 Internal standard stock solution

7.4.3.1 Solution with insulating liquid

A clean dry glass syringe, gas tight, closed by a stainless-steel cap on the tip is prepared by introducing inside four to five glass balls.

The empty syringe is weighed to the nearest 0,001 g or better.

The syringe is filled with the degassed insulating liquid, eliminating the air bubbles through the tip.

The filled syringe is weighed to the nearest 0,001 g or better, and the actual mass of insulating liquid is determined by subtracting the empty syringe weight.

The cap is removed from the syringe tip and, using a GC micro-syringe, an amount of D_6-ethanol is introduced in order to obtain a final concentration of insulating liquid of about 100 mg · kg^{-1}. The syringe is sealed again.

NOTE The preparation of a mother/primary solution of higher concentration (below saturation), from which the internal standard stock solutions can be obtained with a second dilution, is also suitable.

The syringe is shaken gently for 10 min, allowing the glass balls to establish complete homogenization of the spiked insulating liquid.

The actual concentration of the internal standard solution, $[IS]_{liq}$, is determined to four significant digits as follows:

$$[IS]_{liq} = V_{DE} \times \rho / m_{liq}$$

where

V_{DE} is the volume of D_6-ethanol added;

ρ is the density of D_6-ethanol (0,892 g · ml^{-1} at 25 °C);

m_{liq} is the mass of insulating liquid inside the syringe.

The IS stock solution is stored in an amber glass bottle with a polytetrafluoroethylene (PTFE) lined screw cap in a cool environment below 5 °C. The solution is brought to room temperature (≈ 25 °C) prior to its use.

The stability of the IS stock solution is checked by analysing a standard MeOH-EtOH solution (see 7.4.4) at least at each new sample sequence.

NOTE Even if stored appropriately, validation of the IS solution storage period by laboratory investigation is desirable.

7.4.3.2 Solution with DMSO

The IS solution can also be prepared in DMSO which is a solvent very suitable for HS-GC analysis (without any interference).

A clean dry standard volumetric flask with stopper is prepared and the empty flask and stopper are weighed together to the nearest 0,001 g or better.

The flask is filled three quarters with DMSO. Deuterated ethanol and/or deuterated methanol is weighed to the nearest 0,001 g or better into the flask. The flask is filled with DMSO to the mark.

The flask is shaked gently for 10 min to promote a complete homogenization of the spiked liquid.

In order to obtain a final concentration in liquid of about 100 mg · kg^{-1} an extra dilution is needed depending on the primary IS stock solution.

$$[IS]_{liq} = m_{DE} \times V_{liq}$$

where

m_{DE} is the weight of deuterated ethanol and/or deuterated methanol added;

V_{liq} is the volume of DMSO inside the standard flask.

The IS stock solution is stored in an amber glass bottle with a polytetrafluoroethylene (PTFE) lined screw cap in a cool environment below 5 °C. The solution is brought to room temperature (≈ 25 °C) prior to its use.

The stability of the IS stock solution is checked by analysing a standard MeOH-EtOH solution (see 7.4.4) at least at each new sample sequence.

NOTE Even if stored appropriately, validation of the IS solution storage period by laboratory investigation is desirable.

7.4.4 Standard solutions of methanol and ethanol

7.4.4.1 General

These standard solutions can be used for external calibration for the HG-GC-MS method (Method A) analogously to the procedure for HS-GC-FID method (Method B, see 8.9).

7.4.4.2 Standard solutions in insulating liquid

A calibration set of at least five standard solutions in degassed unused insulating liquid is prepared, following the same procedure applied for the IS stock solution (see 7.4.3.1), within a concentration range from 0,01 mg · kg^{-1} to 3,00 mg · kg^{-1} for methanol and for ethanol.

The range of concentrations covered by the prepared standard solutions are within the limit of detection and linearity range of the instrument, and consistent with the expected concentrations of methanol and ethanol in the tested insulating liquids.

NOTE Standard solutions can be prepared from a mother solution in insulating liquid with a concentration of approximately 2 000 mg · kg^{-1}.

The standard solutions are stored in amber glass bottles with polytetrafluoroethylene (PTFE) lined screw caps in a cool environment below 5 °C. The solutions are brought to room temperature (≈ 25 °C) prior to their use.

7.4.4.3 Standard solutions in DMSO

A calibration set of at least five standard solutions in DMSO is prepared, following the same procedure applied for the IS stock solution (see 7.4.3.2), within a concentration range from 0,01 mg · kg^{-1} to 3,00 mg · kg^{-1} for methanol and for ethanol.

The range of concentrations covered by the prepared standard solutions are within the limit of detection and linearity range of the instrument, and consistent with the expected concentrations of methanol and ethanol in the tested insulating liquids.

NOTE Standard solutions can be prepared from a mother solution in insulating liquid with a concentration of approximately 2 000 mg · kg^{-1} (ppm).

The standard solutions are stored in amber glass bottles with polytetrafluoroethylene (PTFE) lined screw caps in a cool environment below 5 °C. The solutions are brought to room temperature (≈ 25 °C) prior to their use.

7.5 Sample preparation

An HS vial is firmly crimped before conditioning with the carrier gas used in the gas chromatograph. Conditioning in accordance with IEC 60567 has been found suitable. Some equipment in the market allow vial conditioning before sealing.

NOTE 1 Vial conditioning avoids the ingress of an excessive amount of air in the MS apparatus preventing consumption of the filament. Otherwise, most MS devices can send to waste the initial portion eluted from the chromatograph; in this case conditioning can be omitted.

Around 7 g ± 0,1 g of the insulating liquid sample is transferred into the vial using a glass syringe equipped with a stainless-steel needle.

NOTE 2 Other liquid amounts in the vial can be used, provided they are compatible with the HS extraction system used.

A quantity of IS stock solution (e.g. 40 µl) is added into the vial such that the final concentration of internal standard in the specimen is close to 0,50 mg · kg^{-1}.

NOTE 3 Other quantities of IS stock solution in the vial can be used, provided they are compatible with the HS extraction system used.

The amount used for the sample testing is the same as for calibration.

If the analyte concentration in the sample is outside the linearity range of the instrument, the dilution is adjusted with a degassed insulating liquid free from MeOH and EtOH, so the final concentration falls within the calibration curve.

7.6 Headspace sampler parameters

The temperature of the sampler oven is set to a range between 40 °C and 85 °C. The vials are heated for 15 min to 30 min with the vial shaking active. A longer time can be applied if it provides better sensitivity.

NOTE 1 Temperature has a great influence on the sensitivity.

The temperature of the transfer line and injection loop (or the precision micro-syringe) is set at an increasing temperature maintained 15 °C lower than the maximum temperature reached by the column during the run, to avoid condensation of sample components.

NOTE 2 Usually the injection loop is at least 10 °C higher than the oven headspace, and the transfer line at least 10 °C higher than the loop. These escalating temperatures avoid sample contamination. However, in the whole system, there is always an oil "contamination" due to the nature of the oil matrix.

Injection volume can be 250 µl to 1 000 µl, depending on the injector type and its internal volume.

On-column injection can be used taking into account the column's capacity with regard to the injected volume. Excessive volume can cause peak tailing.

7.7 Gas chromatograph parameters

7.7.1 Injector

A split/splitless injector can be used to introduce a known amount of sample into the chromatographic system, with parameters chosen to take into account the column capability. The use of an automated injector is preferred.

The injector temperature is maintained 15 °C lower than the maximum temperature reached by the column during the run to avoid condensation of sample components.

If a split technique is used, the best split ratio is determined and optimized based on experience. A suitable ratio can be 5:1 but others can be used if they allow reaching the required detection limit for both methanol and ethanol. A high split ratio reduces sensitivity but also background noise.

7.7.2 Carrier gas

Helium is preferred as carrier gas with 1 ml · min^{-1} flow.

Other flow rates can be applied, provided they allow the complete separation of the analyte peaks.

7.7.3 Temperature ramp

Separation parameters depend on the apparatus used and the temperature ramp is tuned to optimize separation and elution times.

The example of temperature ramp given in Table 1 was found to give satisfactory separation for a 624-type capillary column 30 m × 320 µm.

Table 1 –Method A – Example of GC temperature ramp parameters

Rate ($°C \cdot min^{-1}$)	Temperature (°C)	Final hold (min)	Total runtime (min)
0	40	7	7
10	75	0	10,5
50	300	5	20

Other parameters can be used with other types of columns.

7.8 Mass spectrometer parameters

The MS detector is operated in selected-ion monitoring (SIM) mode, acquiring the signals of ions $\{H_2C\text{-}OH\}^+$ (m/z = 31) and $\{D_2C\text{-}OH\}^+$ (m/z = 33) and the electron energy is set at 70 eV.

NOTE 1 Because the deuterium bonded into the hydroxyl group is readily replaced by a proton, the actual analytes that can be detected in the column eluent are D_3-methanol and D_5-ethanol giving ion $\{D_2C\text{-}OH\}^+$.

NOTE 2 The MS detector can also be operated in total ion current (TIC) mode, extracting the appropriate ions signals in a second step.

Methanol and ethanol peaks can be detected with ions m/z = 31. The internal standard peak can be detected following the values given in Table 2:

Table 2 – Method A – m/z values of internal standard ions

IS analyte	Ion m/z
D_3-methanol	33
D_5-ethanol	33
^{13}C-methanol	32
$^{13}C_2$-ethanol	32

NOTE 3 Slightly different ion m/z values can be used as target and qualifier, after verification and determination with the TIC mode.

Parameters (ionization energy, source temperature, etc.) can be optimized based on the manufacturer's operative instructions.

7.9 Analysis procedure

The HS-GC-MS system is conditioned to a stable baseline.

The sample vial in the HS sampler is heated and the selected amount of gaseous phase of the headspace is injected.

The established temperature ramp is run, the MS detector signal is acquired and stored with suitable data system with peak integration capability.

After the run is completed, the chromatogram is collected with the integrated peak areas of MeOH, EtOH and IS used for the concentration calculation.

An example of a chromatogram is shown in Figure 2 below.

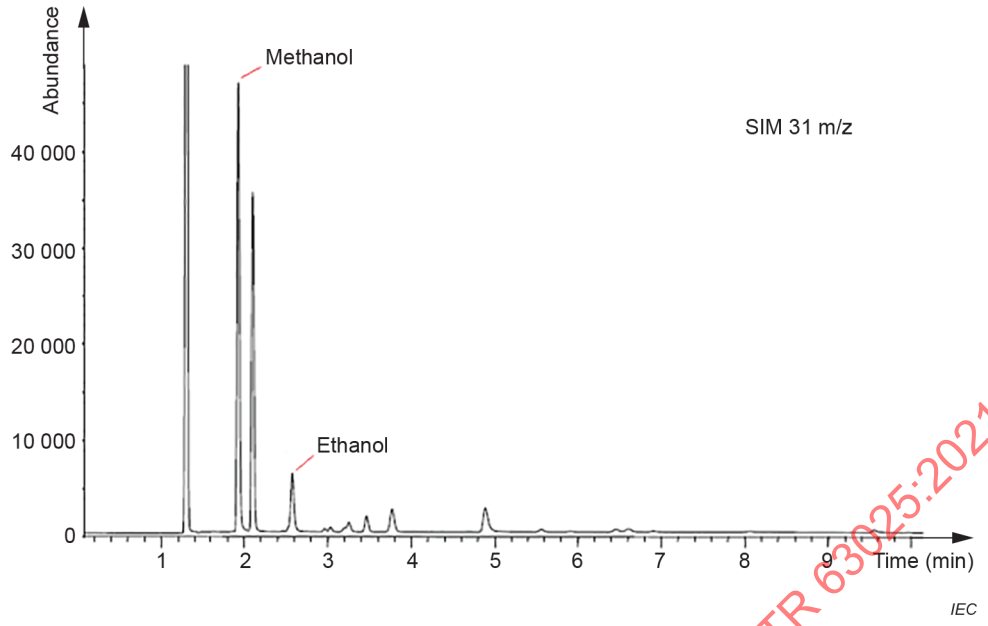


Figure 2 –Typical chromatogram with selected ion (m/z = 31) mass spectrum

Deuterated ethanol (C_2D_5-OH) elutes approximately at the same retention time (RT) as ethanol (C_2H_5-OH), and the related peak is visible with the m/z = 33 ion on the SIM 33 m/z chromatogram.

The analyte concentrations are calculated from the signals obtained for methanol, ethanol and deuterated ethanol peaks, corrected by the response factors (RF) calculated with the calibration procedure (see 7.10 below), using the following equations:

$$[\text{MeOH}] = A_{\text{MeOH}} \times [\text{IS}] / A_{\text{IS}} \times RF_{\text{MeOH}}$$

$$[\text{EtOH}] = A_{\text{EtOH}} \times [\text{IS}] / A_{\text{IS}} \times RF_{\text{EtOH}}$$

where

[XOH] is the concentration of the analyte, methanol or ethanol;

[IS] is the concentration of the internal standard, D_5-ethanol;

A_{XOH} is the area of the peak for a specific analyte;

A_{IS} is the area of the peak for the internal standard;

RF_{XOH} is the response factor for a specific analyte.

7.10 Internal standard calibration

7.10.1 General

Calibration and measurements are carried out with vials of the same size.

The responses of MeOH and EtOH are compared with the response of a known amount of internal standard (D_5-ethanol) based on calibration curves.

NOTE The standard solutions of MeOH and EtOH (see 7.4.4) can also be used for an external calibration in the HG-GC-MS method (Method A) analogously to the procedure for the HS-GC-FID method (Method B, see 8.9).

7.10.2 Response factor determination

The calibration set of standard solutions is prepared with known amounts of methanol and ethanol (see 7.4.4) following the same procedure as for the sample preparation (see 7.5).

The standard solutions are analysed following the analysis procedure of Method A (see 7.9). The analysis is run in triplicate.

The response factor, RF, is calculated as follows:

$$RF_{\text{MeOH}} = A_{\text{MeOH}} \times [\text{IS}] / A_{\text{IS}} \times [\text{MeOH}]$$

$$RF_{\text{EtOH}} = A_{\text{EtOH}} \times [\text{IS}] / A_{\text{IS}} \times [\text{EtOH}]$$

where

RF_{XOH} is the response factor of analyte, methanol or ethanol;

A_{XOH} is the area of the peak for the analyte;

A_{IS} is the area of the peak for the internal standard, D_5-ethanol;

[XOH] is the concentration of the analyte;

[IS] is the concentration of the internal standard, D_5-ethanol.

NOTE Some software packages can produce the inverse of the response factor defined here.

The value of RF is calculated at different concentrations of the two analytes, and its variation along the linearity range should not exceed 5 %.

In the case of higher RF variability, in the result calculation, the RF value obtained for the standard concentration that is closer to the sample concentration is used.

7.11 Expression of the results

The concentrations of methanol and ethanol are reported to the nearest $\mu g \cdot kg^{-1}$.

8 Method B – HS-GC-FID

8.1 General

Method B can be applied using a total oil gas analysis (TOGA) system with parameters adjusted to perform integral analysis of gases and MeOH and EtOH.

Differences between gas chromatographs, headspace samplers and flame ionization detectors from different manufacturers make it impractical to specify detailed operating conditions. Refer to the manufacturer's instructions for instrument setup to allow optimized separation and detection of MeOH and EtOH.

8.2 Apparatus

8.2.1 Analytical balance

A balance with a precision at 4th gram decimal (0,000 1 g) or better is used.

8.2.2 Headspace sampler

HS sampler equipped with an oven capable of heating the HS vials up to 90 °C, running with mechanical shaking. Its injection loop and transfer line are connected to the injection port of the gas chromatographer.

The injection volume is in the range 250 µl to 1 000 µl.

8.2.3 Gas chromatograph with flame ionization detector

A gas chromatograph equipped with a flame ionization detector is used.

A split/splitless injector can be used but other injection techniques are suitable (e.g. on-column).

The use of a porous layer open tubular (PLOT) GC column is necessary to achieve an adequate peak separation and to achieve good detection limits. A capillary column for light alcohols, 30 m to 60 m long, low bleeding, giving the appropriate separation of the analytes and potential interferents is opted for.

8.3 Reagents and materials

8.3.1 Laboratory equipment and glassware

The vessels and accessories used for the tests are cleaned and prepared with analytical grade solvents.

NOTE 1 To ensure that all glassware and accessories are free from MeOH and EtOH, they can be heated in an oven at 100 °C for 1 h to 2 h and brought back to room temperature prior to their use.

- headspace glass vials of 20 ml nominal capacity, with crimp- or screw-type caps and polytetrafluoroethylene (PTFE) faced butyl septa;

NOTE 2 Vials and septa fulfilling the IEC 60567 requirements are suitable.

NOTE 3 Other volumes of vials are suitable (e.g. 10 ml).

- crimping system;
- Class A volumetric flasks;
- volumetric dispensers in a precision class compatible with the required uncertainty of measure. Volumetric dispensers with a precision of ±1 % can be accepted;
- glass syringes, gas tight, 20 ml to 50 ml equipped with three-way glass (stainless steel) or PTFE stopcocks for dosing the insulating liquid during calibration and analysis;
- micro-syringes for gas chromatography of suitable volume (usually 10 µl);
- glass balls of 2 mm diameter for easier solution homogenization.

8.3.2 Standard chemicals

- unused insulating liquid that is free from MeOH and EtOH. To remove residues of MeOH and EtOH, see 8.4.2;
  - mineral oil conforming to IEC 60296 specifications;
  - synthetic esters conforming to IEC 61099 specifications;
  - natural esters conforming to IEC 62770 specifications;
- methanol (CH_4O), analytical grade, anhydrous (purity > 99 %);
- ethanol (C_2H_6O), analytical grade, anhydrous (purity > 99 %).

8.3.3 GC carrier gases

- argon, Ar, purity 5.0 (99,999 %), preferred gas;
- hydrogen, H_2, purity 5.0 (99,999 %);
- synthetic air, purity 5.0 (99,999 %).

8.4 Preparation of standard solutions

8.4.1 General

The insulating liquid used to prepare the standard solutions are of the same type (mineral oil, ester, etc.) as the samples to be tested.

8.4.2 Degassed insulating liquid

A suitable volume of unused insulating liquid is degassed under vacuum (≤ 1 Pa) for 24 h, to remove residual traces of methanol and ethanol.

The objective is for the final insulating liquid to have contents of methanol and ethanol below 10 µg · kg^{-1}.

NOTE This step can be avoided if the unused insulating liquid can be proven to have MeOH and EtOH contents three times lower than the required quantification limits.

8.4.3 Standard solutions of methanol and ethanol

A calibration set of at least five standard solutions is prepared in degassed insulating liquid, within a concentration range from 0,01 mg · kg^{-1} to 3,00 mg · kg^{-1} for methanol and for ethanol, making sure they are within the limit of detection and linearity range of the instrument.

The range of concentrations covered by the prepared standard solutions are consistent with the expected concentrations of methanol and ethanol in the insulating liquids to be tested.

NOTE 1 Standard solutions can be prepared from a mother solution in insulating liquid with a concentration of approximately 8 000 µg · kg^{-1} (ppb).

A clean dry glass syringe, gas tight, closed by a stainless-steel cap on the tip is prepared by introducing inside four to five glass balls.

The empty syringe is weighed to the nearest 0,001 g or better.

The syringe is filled with the degassed insulating liquid, eliminating the air bubbles through the tip.

The filled syringe is weighed to the nearest 0,001 g or better, and the actual mass of insulating liquid is determined by subtracting the empty syringe weight.

The cap from the syringe tip is removed, and using a GC micro-syringe, an amount of methanol (or ethanol) is introduced in order to obtain the targeted concentration of insulating liquid. The syringe is sealed again.

NOTE 2 The preparation of an intermediate solution of known concentration of MeOH and EtOH, from which the standard solutions can be prepared, is also suitable.

The syringe is shaken gently for 10 min, allowing the glass balls to establish a complete homogenization of the spiked insulating liquid.

The actual concentration of the standard solution, $[\text{X-OH}]_{liq}$ is determined to 4 significant digits as follows:

$$[\text{X-OH}]_{liq} = V_{\text{X-OH}} \times \rho_{\text{X-OH}} / m_{liq}$$

where

$V_{\text{X-OH}}$ is the volume of the alcohol, MeOH or EtOH, injected;

$\rho_{X\text{-}OH}$ is the density of the alcohol injected:

MeOH = 0,7910 g · cm^{-3} at 20 °C

EtOH = 0,789 g · cm^{-3} at 20 °C;

m_{liq} is the mass of insulating liquid inside the syringe.

This procedure is repeated for each standard solution of both alcohols.

The standard solutions are stored in amber glass bottles with polytetrafluoroethylene (PTFE) lined screw caps in a cool environment below 5 °C. The solution is brought to room temperature (≈ 25 °C) prior to its use.

8.5 Sample preparation

An HS vial is firmly crimped before conditioning with the carrier gas used in the gas chromatograph. Conditioning in accordance with IEC 60567 has been found suitable. Some equipment in the market allow vial conditioning before sealing.

Around 7 g ± 0,1 g of the insulating liquid sample is transferred into the vial using a glass syringe equipped with a stainless-steel needle.

NOTE Other insulating liquid amounts in the vial can be used, provided they are compatible with the HS extraction system used.

The amount used for sample testing is the same as for calibration.

If the analyte concentration in the sample is outside the linearity range of the instrument, the dilution is adjusted with a degassed insulating liquid free from MeOH and EtOH, so that the final concentration falls within the calibration curves.

8.6 Headspace sampler parameters

The temperature of the sampler oven is set at a range between 40 °C and 85 °C. The vials are heated for 15 min to 30 min with the vial shaking active. A longer time can be applied if it provides better sensitivity.

NOTE 1 Temperature has a great influence on the sensitivity.

The temperatures of the transfer line and injection loop (or the precision micro-syringe) are set at an increasing temperature maintained 15 °C lower than the maximum temperature reached by the column during the run, to avoid condensation of sample components.

NOTE 2 Usually the injection loop is at least 10 °C higher than the oven headspace, and the transfer line at least 10 °C higher than the loop. These escalating temperatures avoid sample contamination. However, in the whole system, there is always an oil "contamination" due to the nature of the oil matrix.

For different HS-GC systems refer to the manufacturer's instructions for instrument setup for methanol and ethanol detection.

Injection volume can be 250 µl to 1 000 µl, depending on the injector type and its internal volume.

On-column injection can be used considering the column's capacity with regard to the injected volume. Excessive volume can cause peak tailing.

8.7 Gas chromatograph parameters

8.7.1 Injector

A split/splitless injector can be used to introduce a known amount of sample into the chromatographic system, with parameters chosen to take into account the column capability. The use of an automated injector is preferred.

The injector temperature is maintained 15 °C lower than the maximum temperature reached by the column during the run to avoid condensation of sample components.

If split technique is used, the best split ratio is determined and optimized based on the experience. A suitable ratio can be 5:1 but others can be used if they allow reaching the required detection limit for both methanol and ethanol. A high split ratio reduces sensitivity but also background noise.

8.7.2 Carrier gas

Argon (Ar) is the preferred carrier gas for Method B. A suitable gas-flow is 10 ml to 15 ml · min^{-1} if a porous layer open tubular (PLOT) type column is used.

Other flow rates can be applied provided that the complete separation of the peaks of the two analytes is ensured.

8.7.3 Temperature ramp

The GC temperature ramp is optimized by each laboratory. Experience suggests to run the analysis with the same ramp usually applied for dissolved gas analyses (see IEC 60567).

8.7.4 FID parameters

The parameters shown in Table 3 depicted in literature have been found to be satisfactory.

Table 3 – Method B – Examples of FID parameters reported in literature

Temperature, °C	**Hydrogen flow rate,** ml · min^{-1}	**Air flow rate,** ml · min^{-1}	**Make-up gas flow rate,** ml · min^{-1}
250	40	450	5 to 15

Parameters can be adjusted to optimize the analyte detection limits.

8.8 Analysis procedure

The GC-FID system is conditioned to a stable baseline.

The sample vial in the HS system is heated and the selected amount of gaseous portion of the headspace is injected.

After the run is completed, the chromatogram with the peak areas is collected.

An example of chromatograms is shown in Figure 3 below.