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TECHNICAL REPORT

colour inside

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

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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- withdrawn,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
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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

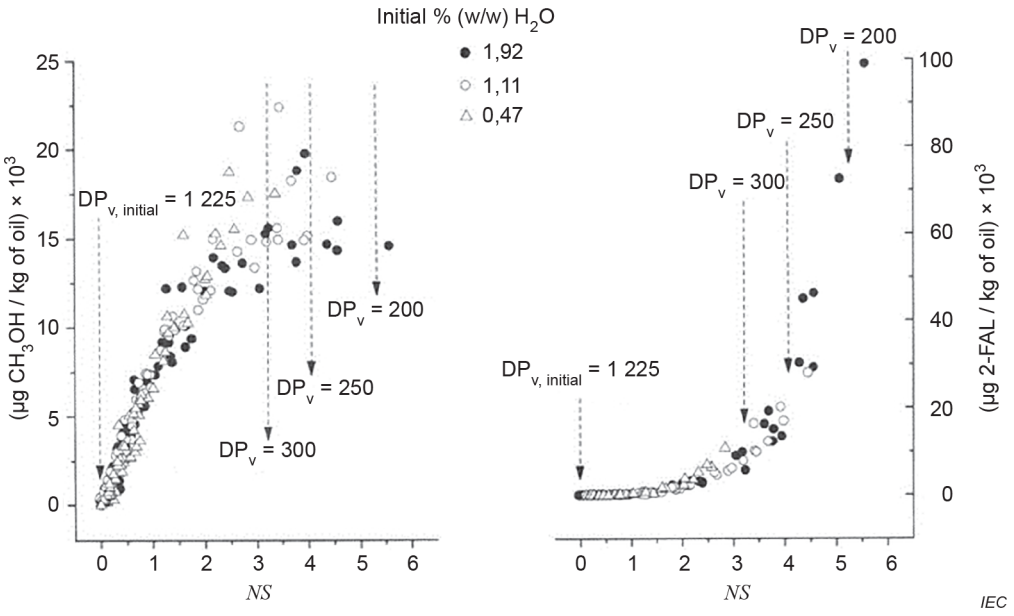
This document does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

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.

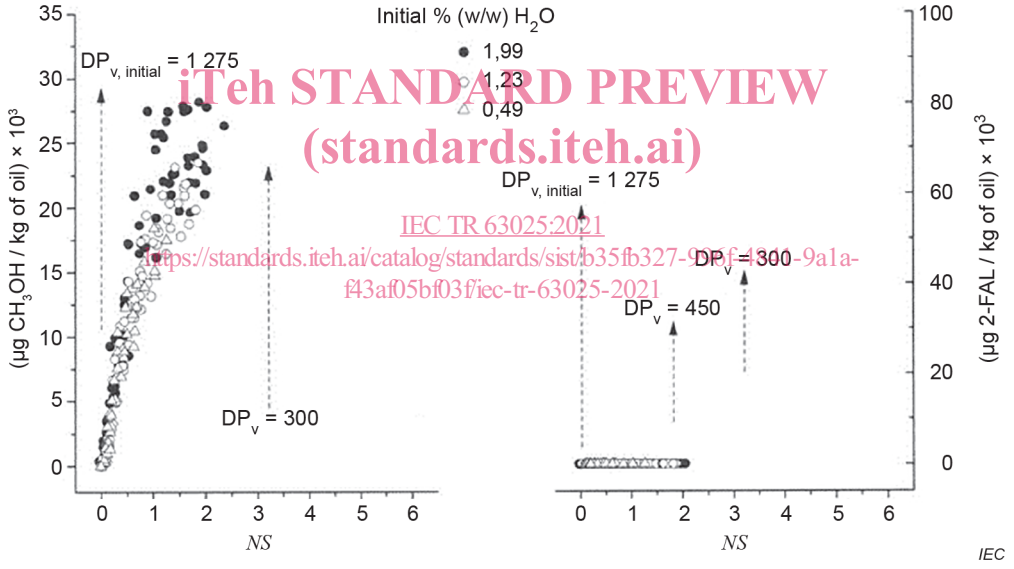
Some of the tests specified in this document involve the use of processes that could lead to a hazardous situation. Attention is drawn to the relevant standard for guidance.

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 4th 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.