Designation: D8086 – 20

Standard Test Method for Determination of Methanol and Ethanol in Electrical Insulating Liquids of Petroleum Origin by Headspace (HS)-Gas Chromatography (GC) Using Mass Spectrometry (MS) or Flame Ionization Detection (FID)[1]

This standard is issued under the fixed designation D8086; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes the determination of by-products of cellulosic materials degradation found in electrical insulation systems that are immersed in insulating liquid. Such materials include paper, pressboard, wood and cotton materials. This test method allows the analysis of methanol and ethanol from the sample matrix by headspace GC-MS or GC-FID.

1.2 This test method has been used to test for methanol and ethanol in mineral insulating liquids and less flammable electrical insulating liquids of mineral origin as defined in D3487 and D5222 respectively. Currently, this method is not a practical application for ester liquids.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D923 Practices for Sampling Electrical Insulating Liquids

D3487 Specification for Mineral Insulating Oil Used in Electrical Apparatus

D3612 Test Method for Analysis of Gases Dissolved in Electrical Insulating Oil by Gas Chromatography

D5222 Specification for High Fire-Point Mineral Electrical Insulating Oils

D5837 Test Method for Furanic Compounds in Electrical Insulating Liquids by High-Performance Liquid Chromatography (HPLC)

3. Terminology

3.1 *Definitions:*

3.1.1 *extract ion mass spectrum, n*—a record that shows a specific mass-to-charge ratio (m/z) extracted from a mass spectrum.

3.1.2 *mass spectrum, n*—a record that shows the relative number of ions of various mass that are produced when a given substance is processed in a mass spectrometer.

4. Summary of Test Method

4.1 Analysis of methanol (CH_3OH) and ethanol (C_2H_5OH) in electrical insulating liquids consists of bringing an insulating liquid sample in contact with a gas phase (headspace) in a closed vessel. The dissolved species contained in the insulating liquid are then equilibrated between the two phases in contact under controlled conditions (according to Henry's law). At equilibrium, the headspace is over-pressurized with a carrier gas and then the content of a loop is filled by the depressurization of the headspace against the ambient atmospheric pressure (see Note 1).

NOTE 1—Other headspace principles may also be used but need to be verified and the analytical performance may be somewhat different than listed.

4.2 The gases contained in the loop or in the syringe are introduced into a gas chromatograph.

4.3 Methanol and ethanol in the test specimen are quantified using calibration curves.

[1] This test method is under the jurisdiction of ASTM Committee D27 on Electrical Insulating Liquids and Gases and is the direct responsibility of Subcommittee D27.03 on Analytical Tests.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

5. Significance and Use

5.1 Methanol and ethanol are generated by the degradation of cellulosic materials used in the solid insulation systems of electrical equipment. More particularly, methanol comes from the depolymerization of cellulosic materials.[3,4,5,6]

5.2 Methanol and ethanol, which are soluble in an insulating liquid to an appreciable degree, will proportionally migrate to that liquid after being produced from the cellulose.

5.3 High concentrations or unusual increases in the concentrations of methanol or ethanol, or both, in an insulating liquid may indicate cellulose degradation from aging or incipient fault conditions. Testing for these alcohols may be used to complement dissolved gas-in-oil analysis and furanic compounds as performed in accordance with Test Methods D3612 and D5837 respectively.

6. Interferences

6.1 Vessels used for this test need to be prepared with solvents containing no trace of methanol and ethanol. Additionally, solvents that can break down into these alcohols must not be used.

7. Apparatus

7.1 Analytical balance capable of weighing to the nearest 0.0001g.

7.2 Headspace sampler either equipped with an injection loop and a transfer line or direct injection with gas-tight syringe connected to the injection port of the gas chromatograph. The sampler must be capable of equilibrating the species of interest in a specific time. The required equilibration time can be minimized by mixing the sample during the equilibration period and this can be achieved by using a sampler equipped with mechanical shaking. A direct injection headspace vial system may also be used.

7.3 Gas chromatograph equipped with a mass spectrometer as described in Table 1 or equipped with FID detector as described in Table 2 (see Note 2).

NOTE 2—This method was developed with He as the carrier gas. Other carrier gases may also be used with this method but must be verified. Analytical performance may be somewhat different than that listed in this method.

7.4 VF-624ms capillary column (60 m × 0.25 mm diameter with a film thickness of 1.4 µm) or DB-624 (60 m × 0.53 mm ID with a film thickness of 3 µm) for the separation of methanol and ethanol. Other columns have been found to be suitable (see Note 3).

NOTE 3—Columns that give adequate peak separation may also be used with this method but must be verified. Analytical performance may be somewhat different than that listed in this method.

TABLE 1 Instrumental Conditions for MS Detection

Headspace Sampler parameters		
Test Specimen	Loop volume	0.5 mL
Shaking	Power	Maximum Level
Temperatures	Sample	90 °C
	Injection loop	150 °C
	Transfer line	175 °C
Pressure	Vial over-pressure	138 kPa
Times	Equilibration	40 min
	Pressurization	0.2 min
	Loop fill	0.12 min
	Loop equilibration	0.25 min
	Injection	6 min
Direct Injection Headspace System parameters		
Test Specimen	2.5 mL	
Oven Temperature	90 °C	
Oven Parameters	Shaking for 40 min	
Syringe Temperature	100 °C	
Gas Chromatograph parameters		
He carrier gas flow	1.0 mL/min for 55 min	
Injector Split/Splitless:	275 °C at 138 kPa	
Split ratio	5 : 1	
Column	60m VF-624ms 0.250 mm dia., 1.4 µm film thickness	
Oven Temp Initial	40 °C for 10 min	
Ramp 1	40 to 275 °C at 20 °C/min	
Hold	275 °C for 33.25 min	
Detector		
Mass Spectrometer	Ionization energy 70 eV Interface at 280 °C m/z = 30-300 in TIC mode at 0.35 scans/s	

TABLE 2 Instrumental Conditions for FID Detection

Headspace Sampler parameters		
Test Specimen	Loop volume	0.5 mL
Shaking	Power	Maximum Level
Temperatures	Sample	90 °C
	Injection loop	150 °C
	Transfer line	175 °C
Pressure	Vial over-pressure	138 kPa
Times	Equilibration	40 min
	Pressurization	0.2 min
	Loop fill	0.12 min
	Loop equilibration	0.25 min
	Injection	6 min
Direct Injection Headspace System parameters		
Test Specimen	2.5 mL	
Oven Temperature	90 °C	
Oven Parameters	Shaking for 40 min	
Syringe Temperature	100 °C	
Gas Chromatograph parameters		
He carrier gas flow:	11 mL/min for 20 min	
Injector Splitless	110 °C megabore direct	
Column	DB-624 60 m × 0.53 mm ID 3 µm film thickness	
Oven Temp Initial	35 °C for 10 min	
Ramp 1	35 to 250 °C at 5 °C/min	
Hold	250 °C for 5 min	
Detector		
FID	Temperature	300 °C
	Hydrogen	40 mL/min
	Air	400 mL/min
	He Makeup	5 mL/min

[3] Jalbert, J., Gilbert, R., Tétreault, P., Morin, B., Lessard- Déziel, D., "Identification of a chemical indicator of the rupture of 1,4-β-glycosidic bonds of cellulose in an oil-impregnated insulating paper system," *Cellulose*, 14:295-309, 2007.

[4] Gilbert, R., Jalbert, J., Tétreault, P., Morin, B., and Denos, Y., "Kinetics of the production of chain-end groups and methanol from the depolymerization of cellulose during the ageing of paper/oil systems," Part 1: Standard wood kraft insulation, *Cellulose*, 16: 327-338, 2009.

[5] Gilbert, R., Jalbert, J., Duchesne, S., Tétreault, P., Morin, B., and Denos, Y., "Kinetics of the production of chain-end groups and methanol from the depolymerization of cellulose during the ageing of paper/oil systems," Part 2: Thermally-upgraded insulating papers, *Cellulose*, 17: 253-269, 2010.

[6] Jalbert, J., Rodriguez-Celis, E., Duchesne, S., Morin, B., Ryadi, M., and Gilbert, R., "Kinetics of the production of chain-end groups and methanol from the depolymerization of cellulose during the ageing of paper/oil systems," Part 3: extension of the study under temperature conditions over 120 °C, *Cellulose*, 22: 829-848, 2015.