Designation: D5837 – 15 (Reapproved 2023)

Standard Test Method for Furanic Compounds in Electrical Insulating Liquids by High-Performance Liquid Chromatography (HPLC)[1]

This standard is issued under the fixed designation D5837; 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 covers the determination in electrical insulating liquids of products of the degradation of cellulosic materials such as paper, pressboard, and cotton materials typically found as insulating materials in electrical equipment. These degradation products are substituted furan derivatives, commonly referred to as furanic compounds or furans. This test method allows either liquid/liquid or solid phase extraction (SPE) of the furanic compounds from the sample matrix followed by analysis for specific furanic compounds by HPLC or direct injection for analysis of specific furanic compounds by HPLC.

1.2 The individual furanic compounds that may be identified and quantified include the following:

5-hydroxymethyl-2-furaldehyde
furfuryl alcohol
2-furaldehyde
2-acetylfuran
5-methyl-2-furaldehyde

1.3 The direct injection method generally has a higher limit of detection, especially for furfuryl alcohol. Greater interference for furfuryl alcohol may be expected when using the direct injection method as opposed to extraction methods.

1.4 This test method has been used to successfully test for furanic compounds in mineral insulating oil, silicone fluid, high fire point electrical insulating oils of mineral origin, askarels, and perchloroethylene-based dielectric fluids.

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

1.6 *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.*

1.7 *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

2.2 *IEC Standard:*[3]

Method 1198 Furanic Compounds Analysis in Mineral Oil Insulating Oil

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *adsorbent, n*—the stationary phase in solid-phase extraction; silica is used as the adsorbent in this test method.

3.1.2 *extract, n*—the liquid phase of a liquid/liquid extraction containing the compound that has been extracted and that will be analyzed.

3.1.3 *liquid/liquid extraction, n*—the preparative step of extraction by mixing nonpolar test specimen with polar solvent to preferentially partition and concentrate polar compounds of interest from an insulating liquid test specimen.

3.1.4 *mobile phase, n*—the carrier liquid phase in an HPLC analytical system used to transfer the prepared test specimen to and through the analytical column and detector; the composition of the mobile phase affects elution time and separation of analytes.

[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.

[3] Available from International Electrotechnical Commission (IEC), 3, rue de Varembé, 1st floor, P.O. Box 131, CH-1211, Geneva 20, Switzerland, https://www.iec.ch.

3.1.5 *solid phase extraction (SPE), n*—a preparative step based on column chromatography, where intermolecular interactions between adsorbent, solvent, and test specimen components are optimized to effect retention of analytes on a solid-phase extraction cartridge, followed by solvent elution from the extraction cartridge.

3.1.6 *ultraviolet (UV), adj*—referring to that region of the electromagnetic spectrum including wavelengths from 10 nm to 380 nm. The UV detectors of most HPLC systems operate in the range of wavelengths from 190 nm to 380 nm.

4. Summary of Test Method

4.1 Furanic compounds in electrical insulating liquids are extracted from a known volume of test specimen by means of a liquid/liquid extraction or solid-phase extraction. A direct injection of the oil also may be used.

4.2 A portion of the extract or an aliquot of the oil is introduced into an HPLC system equipped with a suitable analytical column and UV detector.

4.3 Furanic compounds in the test specimen are identified and quantified by comparison to standards of known concentration.

5. Significance and Use

5.1 Furanic compounds are generated by the degradation of cellulosic materials used in the solid insulation systems of electrical equipment.

5.2 Furanic compounds which are oil soluble to an appreciable degree will migrate into the insulating liquid.

5.3 High concentrations or unusual increases in the concentrations of furanic compounds in oil may indicate cellulose degradation from aging or incipient fault conditions. Testing for furanic compounds may be used to complement dissolved gas in oil analysis as performed in accordance with Test Method D3612.

6. Interferences

6.1 Materials used in the manufacture of the polypropylene tubes and polyethylene frits of some commercially prepared solid-phase extraction columns may interfere with the determination of furanic compounds, such as furfuryl alcohol and 5-hydroxymethyl-2-furaldehyde.

6.2 The use of acetone in any preparative or analytical step will cause accelerated sample decay and may interfere with the accurate determination of 5-hydroxymethyl-2-furaldehyde.

6.3 The use of cellulosic filtering media may serve to adsorb furanic compounds yielding erroneous or unreproducible results, or both.

7. Apparatus

7.1 *High-Performance Liquid Chromatograph (HPLC)*—The required analytical apparatus, an HPLC, consists of an injection device with sample loop, pumping system capable of mixing at least two solvents, reversed phase analytical column, UV detector or detectors with the ability to operate at a minimum of two wavelengths, and a data recording device or integrator.

7.2 It is recommended that a precolumn packed with the same material as the analytical column be used to increase column life and remove interferences.

7.3 Helium sparging of the mobile-phase solvents is recommended in some cases and with some types of HPLC equipment to displace atmospheric gases dissolved in the mobile-phase solvents and to prevent the evolution of air bubbles.

7.4 The analytical apparatus may be heated several degrees Celsius above ambient if necessary to reduce variance in analytical results that may be caused by temperature fluctuations. Operation at ambient temperature or at a controlled temperature of 30 °C to 40 °C has been found satisfactory by some laboratories.

7.5 The following range of HPLC analytical conditions has been found to be satisfactory for extracted test specimens (specific examples are given in the appendix):

Injection Volume	15 µL to 30 µL
Mobile Phase	water/acetonitrile or water/methanol gradient
Flow Rate	0.5 mL/min to 1.5 mL/min
Column Temperature	ambient to 40 °C
Column	3.9 × 300 mm C18 60 to 125A, 4 µm to 10 µm or 4.1 × 150 mm PRP-1 100 A, 5 µm to 10 µm
Gradient	see appendix

NOTE 1—Some laboratories have found it beneficial to filter all mobile phase solvents with a 0.45 µm or smaller polytetrafluoroethylene or nylon filter. Store water in containers shielded from light. Some laboratories use 50 mL of methanol added to 4 L of water to inhibit biological growth.

7.6 The following HPLC analytical conditions have been found to be satisfactory for direct injection of the oil:

Injection volume	20 µL to 30 µL
Mobile phase	acetonitrile/water gradient
Flow rate, initial	0.5 mL ⁄min to 1.0 mL ⁄min
Column temperature	ambient to 30 °C
Column	Waters® Nova-Pak C18 Reversed Phased 300 × 3.9 mm, 60A, 4 µm
Gradient	see Appendix

7.7 For direct injection, a fixed wavelength between 274 nm and 281 nm has been found to provide the best chromatography for all compounds of interest, except furfuryl alcohol, which is best measured with a separate test using a wavelength between 215 nm and 220 nm. Each furanic compound has a characteristic maximum light absorbance occurring within the indicated ranges of wavelengths. Use of variable wavelength or diode array detectors allows the selection of a specific wavelength for each furanic compound. Each laboratory shall select the specific wavelength to yield maximum absorbance for each compound as follows:

Furanic Compound	nm
5-hydroxymethyl-2-furaldehyde	280 to 282
furfuryl alcohol	215 to 220
2-furaldehyde	272 to 280
2-acetyl furan	270 to 280
5-methyl-2-furaldehyde	280 to 292

7.8 After the last compound of interest elutes through the column, increase the acetonitrile or methanol to 100 % of the mobile phase to remove all oil contamination remaining in the analytical column.

7.9 Readjust the solvent ratio of the mobile phase to the initial conditions and allow 10 min to 15 min for the column to come to equilibrium prior to the next injection.

8. Reagents and Materials

8.1 *Acetonitrile*—HPLC grade.

8.2 *2-Acetylfuran*—99 % purity, CAS #1192-62-7.

8.3 *Electrical Insulating Oil*—Virgin oil of mineral origin.

8.4 *2-Furaldehyde*—99 % purity, CAS #98-01-1.

8.5 *Furfuryl Alcohol*—≥98 % purity, CAS #98-00-0.

8.6 *Hexane*—HPLC grade.

8.7 *5-Hydroxymethyl-2-Furaldehyde*—99 % purity, CAS #67-47-0.

8.8 *Methanol*—HPLC grade.

8.9 *5-Methyl-2-furaldehyde*—≥98 % purity, CAS #620-02-0.

8.10 *Silica SPE Column*—Solid-phase extraction column filled with 500 mg of silica.

8.11 *Toluene*—HPLC grade.

8.12 *Vacuum Manifold*—Device to pull vacuum on solid-phase extraction column in order to pass sample and eluent through SPE column.

8.13 *Volumetric Test Tube*—Test tube designed to volumetrically measure in 0.10 mL graduations.

8.14 *Vortex Mixer.*

8.15 *Water*—HPLC grade.

9. Sampling

9.1 Obtain test specimens (insulating fluid samples) in accordance with the procedures for sampling in Practices D923.

10. Preparation of Extraction Standards in Solvent

10.1 Prepare the extraction standards by dilution of a weighed standard compound to a standard volume or by volumetric addition of a standard compound to a standard volume in accordance with either of the procedures described in 10.1.1 or 10.1.2.

10.1.1 *Weight Procedure*—Weigh out 0.100 g ± 5 % of each of the five furanic compounds listed in this test method and record the weight to the nearest 0.1 mg. Dissolve weighed portions into 100 mL of acetonitrile or methanol. Take 1 mL of this solution and add to a clean 1 L volumetric flask. Add 199 mL of either acetonitrile or methanol, using the same solvent as was used earlier to dissolve the weighed portions of the furanic compounds. Bring the solution in the volumetric flask to 1 L with water. Other ratios of solvent to water may be used such as to match that of the initial mobile phase. This solution yields a concentration of about 1 mg/L (1000 µg/L) of each of the furanic compounds. Use the actual mass of each compound to calculate the concentration. Store in a clean, dark plastic container. Do not store in glass.

10.1.2 *Volumetric Addition*—Furanic compounds that are not liquid at ambient temperature should be heated to 35 °C where all of the compounds are in a liquid state. Use a 1 µL syringe to add the indicated volumes of furanic compounds to 10 mL of acetonitrile or methanol. The volumes to be added are as follows:

0.83 µL ± 1 % of 5-hydroxymethyl-2-furaldehyde
0.88 µL ± 1 % of furfuryl alcohol
0.86 µL ± 1 % of 2-furaldehyde
0.91 µL ± 1 % of 2-acetylfuran
0.90 µL ± 1 % of 5-methyl-2-furaldehyde

10.1.2.1 These volumes represent a mass of 1000 µg of each of the five furanic compounds. Add 10 mL of acetonitrile or methanol containing the dissolved volumes of furanic compounds to 190 mL of the same solvent in a 1 L volumetric flask. Bring this solution to 1 L with water. Other ratios of solvent to water can be used such as to match that of the initial mobile phase. The resulting concentration is 1 mg/L (1000 µg/L) for each of the five furanic compounds. Store as indicated in 10.1.1.

11. Preparation of Calibration Standards in Oil

11.1 Prepare standards of furanic compounds in new dielectric liquid which has been tested and shown to have a flat baseline for the range of retention times for the compounds of interest. Mineral oil shall otherwise conform to Specification D3487. Other dielectric liquids should conform with applicable ASTM specifications.

NOTE 2—The same type of dielectric liquid should be used for standard preparation as the dielectric liquid found in the test specimen(s). This test method has been developed for mineral oil, but has been found to be applicable to other dielectric fluids.

11.2 *Volumetric Preparation:*

11.2.1 Use a graduated 1 µL syringe to inject volumes of the five furanic compounds as listed in 10.1.2 into 8 mL of toluene. Dissolve the compounds and add quantitatively to a 1 L volumetric flask. Make sure all compounds are thoroughly mixed.

11.2.2 Dilute the 8 mL of toluene containing furanic compounds to a total volume of 1 L with electrical insulating oil of mineral origin. The solution yields a concentration of 1 mg/L (1000 µg/L) of each of the five furanic compounds. Store as described in 10.1.1.

11.3 *Gravimetric Preparation:*

11.3.1 Weigh out 0.100 g ± 5 % of each of the five furanic compounds and record the weight to the nearest 0.1 mg. Dissolve the weighed portion in toluene and dilute volumetrically to 100 mL in toluene. Mix thoroughly so that all five furanic compounds are dissolved completely.

11.3.2 Volumetrically dilute 1 mL of the toluene solution from 11.3.1 to 1 L using electrical insulating oil of mineral origin. This solution of furanic compounds in oil yields a concentration of about 1 mg/L (1000 µg/L) for each of the furanic compounds. Use the actual mass of each compound recorded in 11.3.1 to calculate the exact concentration in the resulting solution. Store as described in 10.1.1.

12. Liquid/Liquid Extraction Procedure—Method A

12.1 Measure 1 mL to 2 mL of the extraction solvent (methanol, acetonitrile, or methanol/acetonitrile) into 10 mL of the test specimen in a test tube and cap securely. Mix using a vortex mixer for 3 min for acetonitrile or acetonitrile/methanol

extractions or for 1 min to 5 min for methanol extractions. Other ratios of solvent to oil can be used as long as it is verified that the extraction efficiencies are unchanged.

12.2 Allow the two phases to separate. The top phase is the extract, while the bottom phase consists of the nonpolar portion of the test specimen. Separation may be enhanced by centrifugation.

12.3 The extract may be run as is or may be diluted with water so that the resulting ratio of solvent to water is the same as that of the mobile phase used at the start of the HPLC run.

NOTE 3—It has been found that filtering the extract prior to analysis by HPLC prolongs column life. Another effective method of cleanup is to pass the extract through a precolumn. If a precolumn is used, the laboratory needs to verify by experimentation that there is no significant loss of furanic compounds.

13. Solid Phase Extraction (SPE)—Method B

13.1 Insert SPE column(s) into the vacuum manifold and pass 3 mL to 5 mL of hexane through each SPE column under vacuum. Do not dry the column.

13.2 Mix 10 mL of test specimen with 10 mL of hexane and pass through SPE column at a rate no faster than 3 mL/min. Other quantities of oil can be used as long as it is verified that the extraction efficiencies are unchanged.

13.3 Pass 10 mL to 20 mL hexane through the SPE column to rinse out residual oil and dry the column under vacuum for 5 min. Discard all eluates.

13.4 Elute retained compounds from the SPE column using an acetonitrile/water mixture composed of the same proportions as in the HPLC system's mobile phase. (20 % acetonitrile:80 % water has been found to be satisfactory.) Elute no faster than 3 mL/min.

13.5 Collect the first 2.0 mL to 2.5 mL of eluate from the SPE column. Record the volume of eluate collected.

13.6 If the eluate is cloudy, filter the eluate with a 0.5 µm or smaller polytetrafluoroethylene or other inert material micro syringe filter or filter vial prior to insertion for analysis in the HPLC system. Whatever material is used, the laboratory needs to verify that no alternation and no significant loss of furanic compounds occur. Discard the spent SPE cartridge.

14. Calibration

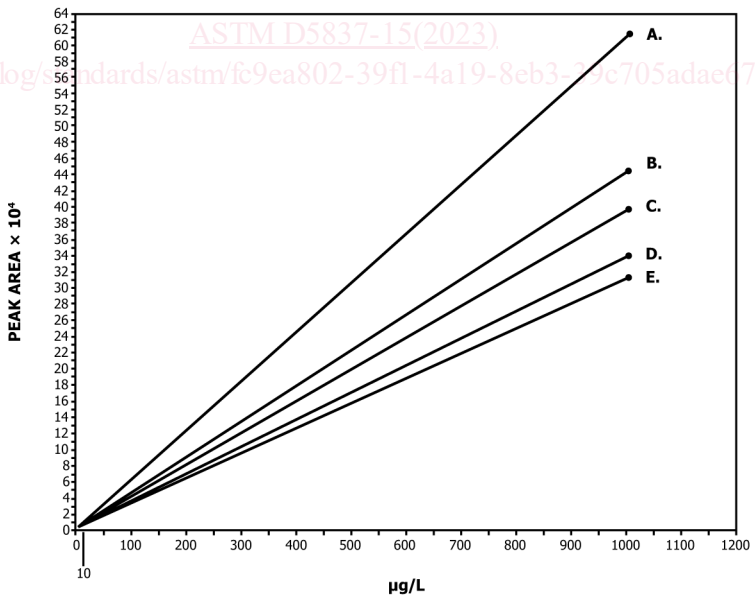
14.1 Calibration consists of development of a calibration curve for each furanic compound, development of extraction efficiencies for each extracted furanic compound, and daily single-point calibration of equipment. Determination of extraction efficiencies is not necessary for the direct injection method.

14.2 *Calibration Curve:*

14.2.1 As appropriate, for each furanic compound, inject an extraction standard in the solvent prepared in accordance with Section 10 to determine the retention time.

14.2.2 Develop a calibration curve for each compound at three separate points representing three orders of magnitude, such as 10 µg/L, 100 µg/L, and 1 mg/L (1000 µg/L) using calibration standards in oil prepared in accordance with Section 11.

14.2.3 Fig. 1 is an example of a calibration curve for each of



Legend:

A.	5-hydroxymethyl-2-furaldehyde
B.	2-furfuraldehyde
C.	5-methyl-2-furaldehyde
D.	2-acetylfuran
E.	furfuryl alcohol

FIG. 1 Example of a Calibration Curve