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Application News

No. L562

High Performance Liquid Chromatography

ASTM D 5837-15 Compliant Quantitative Analysis of Furanic Compound (Furfural) in Transformer Insulation Oil

Insulation oil is a material that is utilized for insulation and cooling of electrical equipment and is widely used in transformers, condensers, and other devices. The concentration of furanic compounds such as furfural in insulation oil is known as an indicator of transformer deterioration. This article introduces a quantitative analysis of furanic compounds in four types of transformer insulation oil using a Shimadzu Prominence™-i integrated LC system, which was conducted in accordance with the furanic compound analysis method provided in ASTM D 5837-15 [1] after the oil samples were subjected to an accelerated deterioration test.

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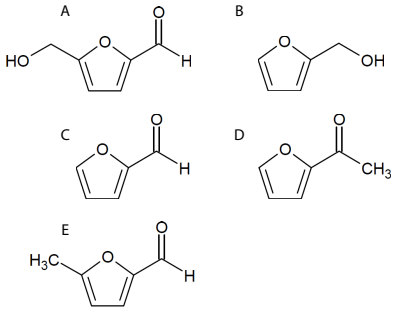
Furanic Compounds in Insulation Oil

Insulation paper is used with insulation oil as an insulation material in transformers. It is known that cellulose, which is the main component of insulation paper, forms several furanic compounds due to the decomposition by operational heat generation and long time usage. Because the concentration of furanic compounds increases as they dissolve into the insulation oil, the concentrations of these compounds are used as an indicator of transformer deterioration. As a method for measuring the furanic compounds in insulation oil, ASTM D 5837 describes a quantitative analysis method for the five types of furanic compounds shown in Fig. 1 by HPLC.



A: 5-hydroxylmethyl-2-furaldehyde (5HMF)
B: furfuryl alcohol (2FOL)
C: 2-furaldehyde (2FAL)
D: 2-acetylfuran (2ACF)
E: 5-methyl-2-furaldehyde (5MEF)

Fig. 1 Structural Formulas of Furanic Compounds

Analysis of Standard Solution of Furanic Compounds

Standard solutions were prepared according to ASTM D 5837 as follows.

A standard solution with a concentration of 1,000 µg/L each of five types of furanic compounds was prepared by dissolving the weighted compounds in acetonitrile to make a constant volume with ultrapure water. Fig. 2 shows the results of an analysis of this standard solution under the conditions in Table 1. Standard solutions with concentrations of 100 µg/L and 10 µg/L were prepared by further diluting the 1,000 µg/L standard solution with ultrapure water, and calibration curves were prepared. Fig. 3 shows the results of the analysis of the 10 µg/L standard solution, and Table 2 shows the correlation coefficient (r^2) of the obtained calibration curve and the limit of quantitation (LOQ) of each component.

Table 1 Analytical Conditions

Column	:	Shim-pack™ VP-ODS (250 × 4.6 mm I.D., 5 µm) *1
Mobile phase	:	A: water B: acetonitrile
Time program	:	B conc. 20% (0-10 min) → 100% (10.01-20 min) → 20% (20.01-40 min)
Flow rate	:	1 mL/min
Column temp.	:	40 °C
Injection vol.	:	15 µL
Detection	:	PDA 220 nm, 280 nm
Vial	:	TORAST-H Glass Vial *2

*1 P/N 228-34937-92
*2 P/N 370-04300-01

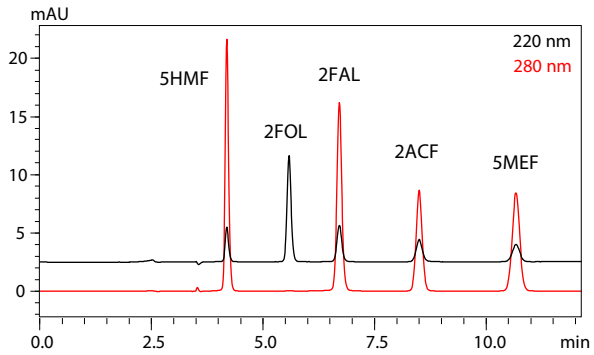


Fig. 2 Chromatograms of Standard Solution (1000 µg/L Each)

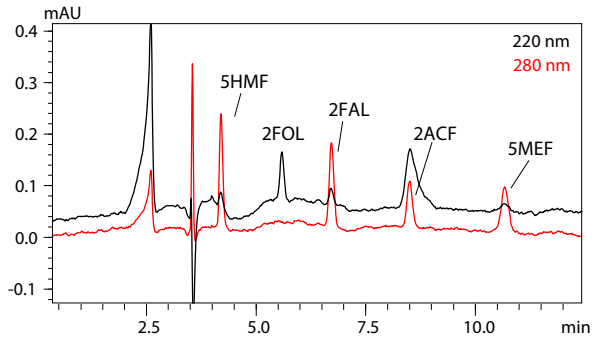


Fig. 3 Chromatograms of Standard Solution (10 µg/L Each)

Table 2 Correlation Coefficient (R^2) of Calibration Curve of Each Component and Limit of Quantitation (LOQ)*

	5HMF	2FOL	2FAL	2ACF	5MEF
Wave length (nm)	280	220	280	280	280
r^2	0.9999	0.9999	0.9999	0.9999	0.9999
LOQ* (µg/L)	1.9	5.7	3.8	6.5	6.2

* Based on the analysis results of the 10 µg/L standard solution, LOQ was obtained by calculating the concentration corresponding to S/N = 10.

Calculation of Extraction Efficiency

Fig. 4 shows the pretreatment protocol for extraction of furanic compounds from insulation oil. The extraction efficiency (*EE*) of each component was calculated by the *EE* calculation method shown in Fig. 5 using a control solution. First, the five types of furanic compounds were weighed and dissolved in toluene, then a 1,000 µg/L control solution was prepared by adding the furanic compounds to white mineral oil. This solution was pretreated by the protocol shown in Fig. 4, and the obtained extraction sample was subjected to the HPLC analysis. Table 3 shows the obtained *EE* values. The repeatability of the analyses including pretreatments was verified by carrying out the pretreatment in Fig. 4 six times. Good extraction efficiency of approximately 90% was obtained for each of the five types of furanic compounds, and the repeatability of the analysis including the pretreatment was approximately 3% as %RSD.

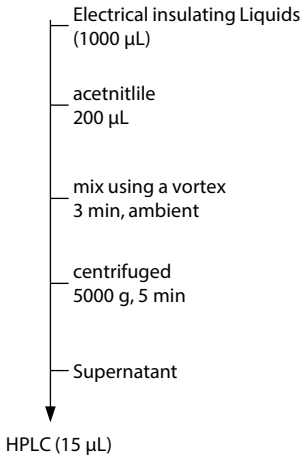


Fig. 4 Pretreatment Protocol

$$EE,(\%) = (R_O/R_S) \times (V_E/1000) \times 100$$

EE = extraction efficiency as a percentage
R_O = peak area of calibration standard in oil at 1000 µg/L
R_S = peak area of extraction standard (1000 µg/L)
V_E = volume of solvent used for extraction (200 µL)
1000 = oil volume (µL)

Fig. 5 Formula for Calculation of Extraction Efficiency (*EE*)

Table 3 Extraction Efficiency (*EE*) and Repeatability (n = 6) of Each Component

	5HMF	2FOL	2FAL	2ACF	5MEF
EE(%)	89.4	94.6	96.3	94.3	96.9
%RSD	3.3	2.0	0.7	0.6	0.6

Analysis of Furanic Compounds in Real Samples

An accelerated deterioration test of four types of insulation oil was conducted by allowing the samples to stand at 150 °C for 48 h or 96 h. After sample pretreatment by the protocol in Fig. 4, an HPLC analysis was carried out to quantify the concentrations of the furanic compounds contained in each of the real samples. Fig. 6 shows the chromatograms of 48 h heat-treated Sample 2 as one example of the obtained chromatogram.

Table 4 shows the calculated concentrations of the furanic compounds in each sample obtained from the *EE* of each component. The results confirmed that elevated levels of some furanic compounds were observed in the sample of Sample 2 subjected to the long-term (96 h) accelerated deterioration test.

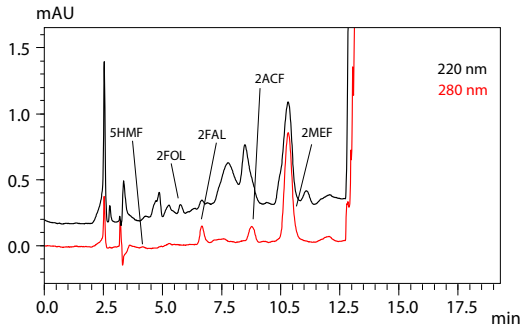


Fig. 6 Chromatograms of Sample 2 Heat-Treated for 48 h

Table 4 Quantitative Values of Furanic Compounds Contained in Samples[*1] (µg/L)
(Red: Components in which increases were confirmed.)

	heating time (hr)	5HMF	2FOL	2FAL	2ACF	5MEF
Sample 1	48	0.1[*2]	2.6	5.4	7.8	45.3
	96	N.D.	4.2	5.5	9.0	37.3
Sample 2	48	0.1[*2]	1.7[*2]	3.0	6.7	40.3
	96	0.1[*2]	3.1	6.0	8.0	49.5
Sample 3	48	N.D.	4.4	4.5	6.9	43.9
	96	0.1[*2]	2.9	4.8	8.5	46.1
Sample 4	48	N.D.	2.9	3.6	3.3	44.2
	96	0.1[*2]	2.1	3.2	5.9	35.6

*1 None of the furanic compounds were detected in the results of the analysis of the control sample (white mineral oil) which was not heat-treated.
*2 Should be considered reference values, as they were obtained by extrapolation from the calibration curve.

Conclusion

An ASTM D 5837-compliant analysis of the furanic compounds in transformer insulation oil was conducted using a Shimadzu Prominence-i integrated HPLC system. Satisfactory recovery ratios and repeatability were confirmed with the assigned pretreatment. In addition, elevated levels of furanic compounds due to oil degradation were confirmed from the results of the analyses of various transformer insulation oils after an accelerated deterioration test.

<References>
(1) ASTM D 5837-15, Standard Test Method for Furanic Compounds in Electrical Insulating Liquids by High-Performance Liquid Chromatography (HPLC)

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