Application News

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Electric insulating oil / ASTM D 5837 HPLC Method

Quantitative Analysis of Furanic Compounds in Transformer oil by HPLC Method

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❑ Introduction

Monitoring the conditions of power transformers is very important to maintain the reliability of industrial power system operations. One critical risk assessment is the quality of the insulation system which consists of insulation paper immersed in insulation oil. The life of the paper insulation determines normally the life of the transformer. Incipient faults within a transformer can be detected by analyzing furanic compounds in insulation oil. Furan analysis in transformer oil, especially the amount of 2-furaldehyde in oil (usually the most prominent of paper decomposition), indicates the degree of degradation of the transformer paper insulation. In this application news, the ASTM D 5837 Test Method [1] was followed for the quantitative analysis of furan derivatives in transformer oil. Five furanic compounds were quantified by HPLC analysis after the samples of transformer oil were extracted by liquid/liquid extraction procedure using acetonitrile.

❑ Experimental

A. Preparation of standards

5-hydroxylmethyl-2-furaldehyde (5HMF), furfuryl alcohol (2FOL), 2-furaldehyde (2FAL), 2-acetylfuran (2ACF) and 5-methyl-2-furaldehyde (5MEF) standards of 98% to 99% purity were obtained from Sigma Aldrich. These five individual furanic standard stock solutions were prepared with toluene. A 5 mixed standard was then prepared from the individual stock solutions using toluene as the diluent. HPLC grade acetonitrile and fresh transformer oil obtained from Sigma Aldrich were used for the serial dilution of the 5 mixed standard to obtain the neat and pre-spiked standards, respectively.

B. Analytical conditions

Prominence™ high performance liquid chromatography (HPLC) system with SPD-M20A diode array detector was employed in this work. The details of HPLC analytical conditions are shown in Table 1.

C. Liquid-liquid extraction – Method A

Two samples of transformer oil were obtained from a power supply company for furan analysis. Liquid-liquid extraction was used with the pre-spiked standards and transformer oil samples by adding 1 mL of ACN to 4 mL of each of the pre-spiked standards or samples. The solution was further vortex-mixed for 3 min, and centrifuged at 5,000×g for 5 min at 25°C. The

top phase is the extract, which will be directly injected into the HPLC system for analysis. The extraction efficiencies (EE) from simulated transformer oil was calculated using the equation as follows:

$$EE\ (\%) = \frac{R_o}{R_s} \times \frac{1}{4} \times 100$$

R_o: average of the integrated peak area of calibration standard pre-spiked in transformer oil
R_s: average of the integrated peak area of calibration standard pre-spiked in solvent

Table 1. Analytical conditions of furanic compounds on HPLC

Column	Shim-pack™ GISS (250 mm L x 4.6 mm I.D., 5µm)		
Mobile Phase	A: Milli-Q® H_2O B: ACN		
Elution Program	Gradient elution		
	Time (min)	A (%)	B (%)
	0.00	85	15
	9.50	85	15
	9.51	0	100
	12.00	0	100
	12.01	85	15
Flow Rate	1.0 mL/min		
Oven Temp.	40°C		
Injection	5 µL		

❑ Results and Discussion

A. HPLC chromatogram

Figure 1 shows chromatograms of a 5 mixed standards of furanic compounds. The total run time is 16 min with the last peak eluting at about 8.9 min.
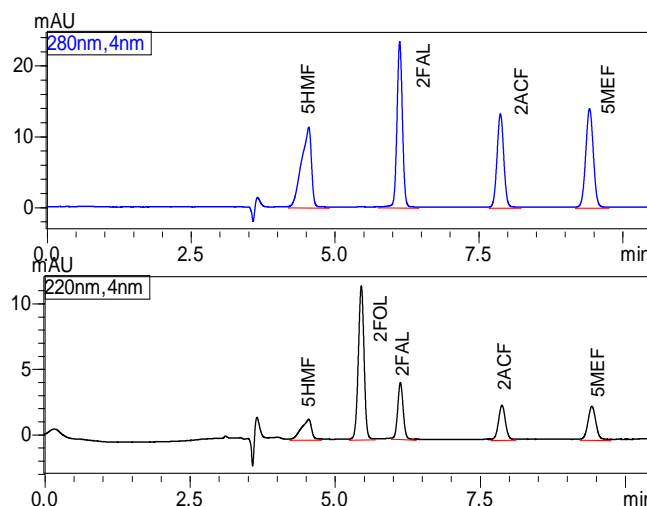

Fig 1. Representative chromatograms of a mixed standard of furanic compounds, 1000 µg/L each spiked in transformer oil.

Table 2. Calibration curves and performance of HPLC method for quantitative determination of five furanic compounds

Furanic compound	Wavelength (nm)	RT (min)	Conc. Range (µg/L)	R²	LOD (µg/L)	LOQ (µg/L)	RSD % (n=3)			Extraction Efficiencies (%) (n=3)		
							500 µg/L	1000 µg/L	9000 µg/L	50 µg/L	1000 µg/L	9000 µg/L
5-hydroxylmethyl-2-furaldehyde (5HMF)	280	4.38	50 ~ 9000	0.999	4.1	12.4	4.7	1.4	1.4	100.5 ± 8.1	102.8 ± 3.2	95.4 ± 3.3
Furfuryl alcohol (2FOL)	220	5.26	50 ~ 9000	0.999	6.7	20.2	1.8	1.3	1.8	94.9 ± 7.2	96.9 ± 1.3	89.8 ± 2.8
2-furaldehyde (2FAL)	280	5.92	50 ~ 9000	0.999	2.0	6.0	4.0	0.6	1.7	90.8 ± 4.9	91.5 ± 1.2	83.4 ± 1.8
2-acetylfuran (2ACF)	280	7.46	50 ~ 9000	0.999	3.5	10.4	5.0	5.7	1.1	88.7 ±10.8	89.5 ± 2.4	80.2 ± 1.7
5-methyl-2-furaldehyde (5MEF)	280	8.89	50 ~ 9000	0.999	3.5	10.7	3.3	1.2	1.0	89.8 ± 7.7	90.9 ± 4.3	81.2 ± 1.9

B. Calibration curves

Seven-point external standard calibration curves were established as displayed in Figure 2. The details of calibration parameters and method performance are shown in Table 2. All the calibration curves shown in Figure 2 exhibit a good linearity with R^2 value of 0.999. The lowest concentration level of 50 µg/L was used to determine sensitivity based on S/N ratios of 3 and 10 for LOD and LOQ, respectively. The results indicate that the sensitivity of the method is sufficient for detection and quantitation of the furanic compounds following ASTM D 5837. Repeatability test was conducted with 50 µg/L (low), 1000 µg/L (med.) and 9000 µg/L (high). The RSD % obtained ranges at 0.6~5.7% as shown in Table 2. The extraction efficiencies obtained were in acceptable range, from 80 to 120 %.
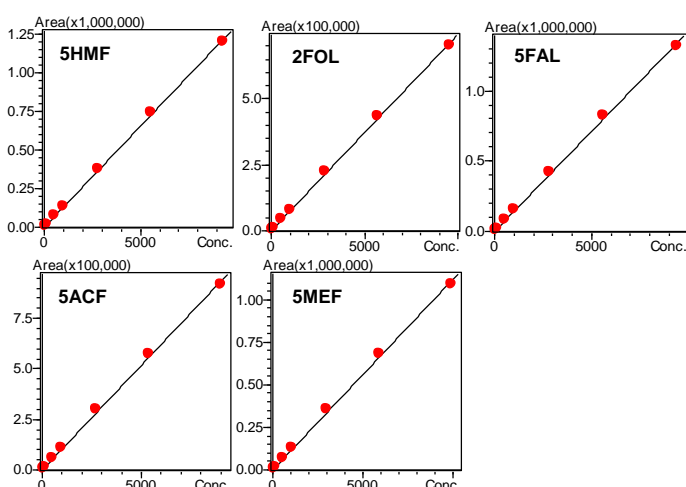

Fig 2. Calibration curves of furanic compounds standards (50 µg/L ~ 9000 µg/L), each pre-spiked in transformer oil

C. Quantitation of unknown transformer oil

Two generator transformer oil samples (TO5 and TO6) were analysed using the method established. The HPLC results are displayed in Figure 3 and the quantitative results are summarized in Table 3. The main furanic compound found is 2-furaldehyde.
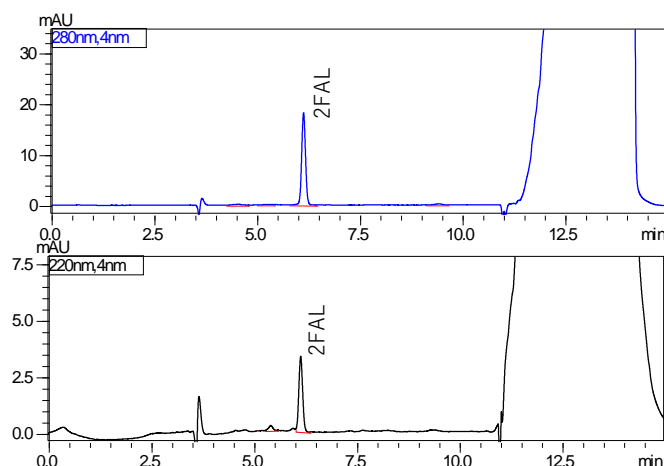

Datafile Name:GT6_001.lcd
Sample Name:GT6
Sample ID:unknow n

Fig 3. HPLC chromatogram of transformer oil sample TO6

Table 3. Quantitative results of furanic compounds in two transformer oil samples

Furanic compounds	Concentration (µg/L)	
	TO5	TO6
5-hydroxylmethyl-2-furaldehyde (5HMF)	<50	<50
Furfuryl alcohol (2FOL)	<50	<50
2-furaldehyde (2FAL)	1170.5	826.7
2-acetylfuran (2ACF)	Not detected	Not detected
5-methyl-2-furaldehyde (5MEF)	<50	<50

❏ Conclusions

A HPLC method was established for quantitative analysis of 5 furanic compounds (5-hydroxylmethyl-2-furaldehyde, furfuryl alcohol, 2-furaldehyde, 2-acetylfuran and 5-methyl-2-furaldehyde) in transformer oil. The sensitivities for the five furanic compounds are sufficient and meet the requirement in ASTM D 5837-99 Standard.

❏ References

1. ASTM D 5837-99 Standard Test Method for Furanic Compounds in Electrical Insulating Liquids by High Performance Liquid Chromatography

❏ Acknowledgement

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