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Application News

No. L576

High Performance Liquid Chromatography

Simultaneous Analysis of Benzotriazole, Tolutriazole Derivatives and Furanic Compounds: Passivators in Insulating Oil

In transformers and condensers, insulating oil and paper are used to insulate conductors and cool the interior of electrical devices. These insulators are degraded by long-term operation or exposure to heat, which can lead to device failure. Accordingly, these insulators should be inspected periodically for to monitor the degradation of the device. Although insulating paper fixed to the device is difficult to remove, the insulating oil easy to collect is analyzed to verify device status.

As one of the test methods, the amounts of additive compounds need to be quantified. Benzotriazole (1, 2, 3-benzotriazole: hereinafter called BTA) and tolutriazole derivative (N-bis[2-ethylhexyl]-aminomethyltolutriazol: hereinafter called TTAA) are added as passivators (metal deactivator) to insulating oil. Determination of BTA and TTAA is required because whether these passivators are added in insulating oil affect the risk of a degradation, such as sulfidation corrosion. The British Standards (BS148:2009) specify test methods of these passivators using the HPLC method.

The ingredient of insulating paper used as a coating for windings in tranformers and condensers is cellulose. Cellulose is decomposed at high temperatures due to device operation and by the water or oxygen contained in degraded insulating oil. Decomposed cellulose is dissolved as furanic compounds in the insulating oil. Thus, the concentrations of furanic compounds in insulating oil are used as indicators of degradation of electrical equipment. This analysis using the HPLC method is specified by the ASTM D5837-15 standards.

On the basis of the methods specified by ASTM and BS, we optimized the test method for passivators and furanic compounds so that these compounds could be analyzed simultaneously. This article introduces simultaneous analysis of BTA, TTAA and furanic compounds in insulating oil using an integrated HPLC system "Prominence™-i".

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Analysis of Standard Mixture

Fig. 1 shows the structural formulas of BTA, TTAA and furanic compounds. The standard mixture was prepared based on ASTM standards. Five furanic compounds, BTA and TTAA were weighed individually, dissolved in acetonitrile, and then diluted with water. Because the analytical standard does not exist for TTAA, commercially available Irgamet® 39* (manufactured by BASF) was used, as noted in BS.

Table 1 shows the analytical conditions, and Fig. 2 shows the chromatograms of the standard mixture. TTAA had two separate peaks because this substance is a mixture of two isomers. In this quantitative analysis, in accordance with BS, the total value of peak areas of these two isomers was used.

Table 2 shows the detection wavelengths and r^2 values for the components. Calibration curves were prepared based on 5 points using the standard mixture solution for BTA and TTAA in the concentration range of 100 - 20000 µg/L and for five furanic compounds in the concentration range of 5 - 1000 µg/L. Good linearity was obtained for the calibration curves of all components.

Table 1 Analytical Conditions

System	: Prominence-i
Column	: Shim-pack™ VP-ODS*1 (250 mm × 4.6 mm I.D., 5 µm)
Mobile Phase	: A) Water, B) Acetonitrile
Time Program	: B conc. 15-45% (0-10 min) → 100% (10.01-20 min) → 15% (20.01-30 min)
Flow Rate	: 1.0 mL/min
Column Temp.	: 40 °C
Injection Vol.	: 15 µL
Vial	: LabTotal Vial kit for LC/LCMS*2
Detection	: PDA 220 nm, 260 nm, 280 nm

*1 P/N: 228-34937-92
*2 P/N: 227-34001-01

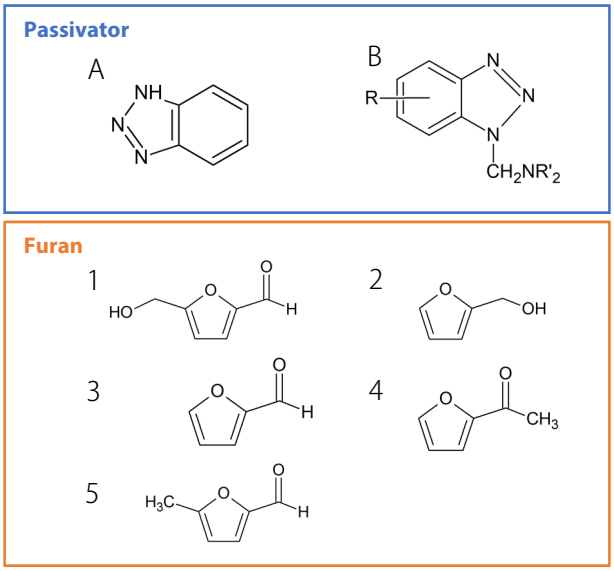

Fig. 1 Structural Formulas
A: BTA, B: TTAA, 1: 5-hydroxylmethyl-2-furaldehyde (5HMF)
2: furfuryl alcohol (2FOL), 3: 2-furaldehyde (2FAL)
4: 2-acetylfuran (2ACF), 5: 5-methyl-2-furaldehyde (5MEF)

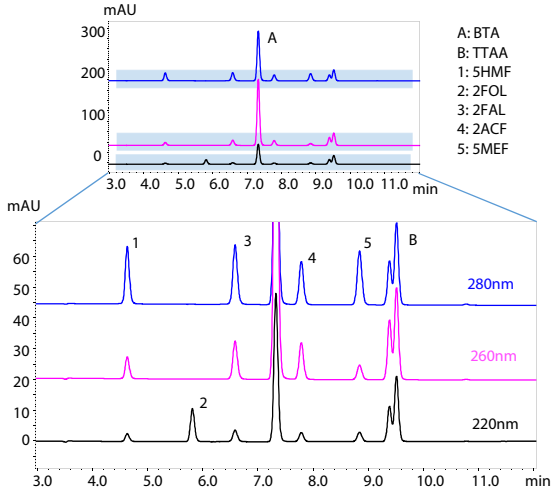

Fig. 2 Chromatograms of Standard Mixture (20000 µg/L of Each of BTA and TTAA, 1000 µg/L of Each Furanic Compound)

Table 2 Detection Wavelengths and r^2 values for All Compounds

	BTA	TTAA	5HMF	2FOL	2FAL	2ACF	5MEF
Wavelength (nm)	260	260	280	220	280	280	280
r^2	>0.9999	>0.9999	>0.9999	>0.9999	>0.9999	>0.9999	>0.9999

Sample Pretreatment and Recovery Test

The samples were pretreated based on the ASTM method as shown in Fig. 3. For the recovery test, BTA, TTAA, and furanic compounds were dissolved in toluene, and then spiked with white oil to calculate the recovery. Table 3 shows the results of the recovery test and reproducibility of pretreatment.

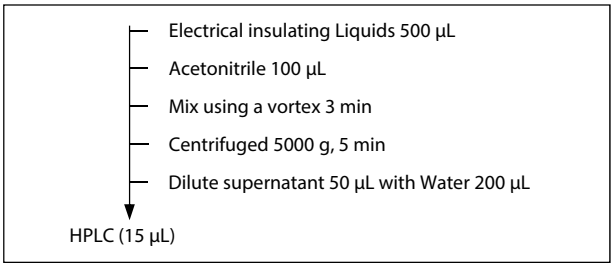

Fig. 3 Pretreatment Protocol

Table 3 Recovery and Reproducibility for Compounds (n=3)

	BTA	TTAA	5HMF	2FOL	2FAL	2ACF	5MEF
Recovery (%)	80	79	122	115	111	109	106
%RSD	1.6	1.9	1.2	1.2	1.2	1.1	1.2

BTA, TTAA and Furanic Compounds in Insulating Oil

The accelerate aging test was conducted for 4 types of insulating oil at 150 °C for 48 hours or 96 hours. After being pretreated individually, as shown in Fig. 3, these samples were analyzed by the HPLC method to determine the concentrations of BTA, TTAA and furanic compounds in the samples.

Fig. 4 shows the chromatograms of Sample 3, in which BTA was detected. The chromatograms are those of Sample 3 heated for 48 and 96 hours and those of Sample 3 pretreated after heating for 96 hours and then spiked with the standard mixture to make up 400 µg/L of each of BTA, TTAA and 20 µg/L of each of the furanic compounds. Table 4 shows the concentrations of these compounds in the samples.

Table 4 The concentrations of BTA, TTAA and Furanic Compounds in the Samples (µg/L)

Sample No.	heating time (hr)	BTA	TTAA	5HMF	2FOL	2FAL	2ACF	5MEF
1	48	N.D.	N.D.	N.D.	N.D.	7.0	23	4.0*
	96	N.D.	N.D.	N.D.	N.D.	9.0	33	3.9*
2	48	N.D.	N.D.	N.D.	N.D.	8.4	26	3.6*
	96	N.D.	N.D.	N.D.	N.D.	9.5	25	4.3*
3	48	140	N.D.	N.D.	N.D.	8.8	29	5.2
	96	190	N.D.	N.D.	N.D.	10	27	5.3
4	48	N.D.	N.D.	N.D.	N.D.	9.0	50	4.1*
	96	N.D.	N.D.	N.D.	N.D.	8.9	21	4.2*

* Provided for reference purposes only because the actual values are not within the range of calibration curves
N.D. = not detected

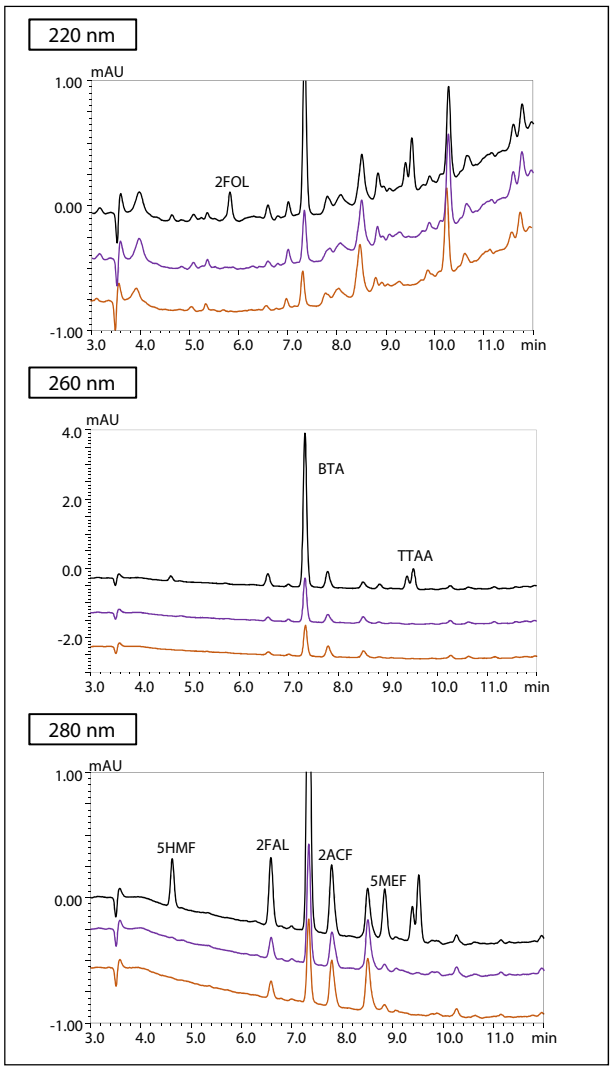

Fig. 4 Chromatograms of Sample 3 Detected at 220 nm, 260 nm and 280 nm

- Heated for 96 hours + spiked with 400 µg/L of each of BTA and TTAA, and 20 µg/L of each of the furanic compounds
- Heated for 96 hours
- Heated for 48 hours

Conclusion

We demonstrated that the passivators and furanic compounds in insulating oil can be analyzed simultaneously by optimizing the test method for furanic compounds specified by the ASTM standards. Although the ASTM and BS standards specify respective analysis of passivators and furanic compounds, simultaneous analysis of these compounds can reduce the time required for analysis. Simultaneous analysis also confirmed that the target compounds can be readily separated from the impurities in insulating oils.

*Irgamet® 39 was provided by BASF Japan Ltd.

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