「Application Note」

Analysis of Furanic Compounds in Transformer Oil (Insulating Oil) by YL9100 Plus HPLC According to ASTM D5837

- HPLC Application

Abstract

As the number of aged transformers is getting increased worldwide, it is important to estimate their remaining lifetime in order to prevent premature shutdown of transformers. And the life of a power transformer mainly depends on the condition of the insulating paper. The most accurate method for evaluating the degradation of insulating paper in a transformer is to measure its degree of polymerization, but it is impossible to directly check the inside of the transformer in operation. Therefore, the evaluation can be conducted by analyzing furanic compounds which are generated by the degradation of cellulosic materials used in the insulating paper to make a decision for transformer replacement and maintenances.

For 2-Furaldehyde is the most common furan compound which is originately generated in the insulating paper, it is a major indicator that can determine the cellulose degradation. Generally, 0 to 100ppb 2-furaldehyde is good, 101 to 250ppb is caution, and if it exceeds 250ppb, it is judged as abnormal.

In this study, 5 kinds of furanic compounds were analyzed by YL9100 Plus HPLC/PDA according to ASTM D5837 method.

Instruments and Software

Item	Description	Part No.
HPLC System	YL9101 Vacuum Dagasser	5611011000
	YL9110 Plus Quaternary Gradient Pump	9361011120
	YL9150 Plus LC Autosampler	9551011000
	YL9131 Plus Column Compartment	5511011050
	YL9160 Plus Photo Diode Array Detector	2201011000
Install.Option	HPLC Performance Kit	1601011890
CDS	YL-Clarity sofrware for single instrument of YL HPLC	5301011000
	PDA module of YL-Clarity	5301011070
	Autosampler control of YL-Clarity	5301011040
Column	C18 (4.6 mm x 250 mm, 5 µm)	-

YL9100 Plus HPLC

Reagents and Standards

- Acetonitrile (CH_3OH), HPLC Grade
- 2-Acetylfuran, 99% purity
- Electrical insulating oil, virgin oil of mineral origin
- 2-Furaldehyde, 99% purity
- Furfuryl alcohol, 99% purity
- Hexane, HPLC grade
- 5-Hydroxymethyl-2-furaldehyde, 99% purity
- Methanol, HPLC grade
- 5-Methyl-2-furaldehyde, 99% purity
- Toluene, HPLC grade
- Ultrapure water
- Silica SPE Column, Solid phase extraction column filled with 500 mg of silica

Table 1. Standard Information

Fomulas and Physical Properties of Furanic Compounds		
Compound	**Formula**	**Molecular weight**
5-Hydroxymethyl-2-furaldehyde	$C_6H_6O_3$	126.11
Furfuryl alcohol	$C_5H_6O_2$	98.10
2-Furaldehyde	$C_5H_4O_2$	96.08
2-Acetyl furan	$C_6H_6O_2$	110.11
5-Methyl-2-furaldehyde	$C_6H_6O_2$	110.11

Preparation of Extraction Standards in Solvent

1. *Weight Procedure*

① Weigh out 0.001g ± 5% of each of the five furanic compounds in the standard and dissolve weighed portions into 100 mL of acetonitrile or methanol.

② Take 1 mL of solution ① and add to a 1 L volumetric flask. Add 199 mL of the same solvent as was used to dissolve the weighed portions of furanic compounds.

③ Take solution ② in the volumetric flask to 1 L with water.

④ Store this solution (1000 µg/L) in a dark plastic container not in glass.

2. *Volumetric Addition*

① Furanic compounds that are not liquid at ambient temperature should be heated to 35°C.

② Use a 10 µL pipette to add the indicated volumes of furanic compounds to 100 mL of acetonitrile of methanol.

5-Hydroxymethyl-2-furaldehyde: 8.3 µL ± 1%

Furfuryl alcohol: 8.8 µL ± 1%

2-Furaldehyde: 8.6 µL ± 1%

2-Acetylfuran: 9.1 µL ± 1%

5-Methyl-2-furaldehyde: 9.0 µL ± 1%

③ Add 10 mL of solution ② and the 190 mL of the same solvent as was used to dissolve the weighed portions of furanic compounds in a 1L volumetric flask.

④ Add water to solution ③ up to 1L.

⑤ Store this solution (1000 µg/L) in a dark plastic container not in glass.

Preparation of Calibration Standards in Oil

1. *Volumetric Preparation*

① Furanic compounds that are not liquid at ambient temperature should be heated to 35°C.

② Add the indicated volumes of furanic compounds to 80 mL of toluene and dissolve them completely.

5-Hydroxymethyl-2-furaldehyde: 8.3 µL ± 1%

Furfuryl alcohol: 8.8 µL ± 1%

2-Furaldehyde: 8.6 µL ± 1%

2-Acetylfuran: 9.1 µL ± 1%

5-Methyl-2-furaldehyde: 9.0 µL ± 1%

③ Take 8ml of solution ② and add it into a 1L volumetric flask. And dilute it to a total volume of 1L with the insulating oil.

④ Store this solution (1000 µg/L) in a dark plastic container not in glass.

2. *Gravimetric Preparation*

① Weight out 0.100g ± 5% of each of the five furanic compounds and dissolve them into 100 mL of toluene.

② Take 1 mL of solution ① and put it in a 1L volumetric flask. Dilute it to a total volue of 1L with the insulation oil.

③ Store this solution (1000 µg/L) in a dark plastic container not in glass.

Preparation of samples

1. Liquid/Liquid Extraction

① Add 2 mL of the extraction solvent (Acetonitrile or Methanol) and 10 mL of sample into a test tube.

② Mix them with a Vortex mixer for 3 min and centrifuge them with a centrifuge.

③ The extract may be run as is or may be diluted with water.

2. Solid Phase Extraction(SPE)

① Insert SPE column into the vacuum manifold and run 5mL of hexane through the column.

② Mix 10 mL of sample with 10mL of hexane. Run the mixed solution throught the SPE column at a rate no faster than 3 mL/min.

③ Pass 20 mL of hexane through the SPE columne to rince out the residual oil at a rate no faster than 3mL/min.

④ Dry the coluln under vacuum for 5 min.

⑤ Elute retained compounds from SPE column with an acetonitrile/water mixture(20% acetonitrile : 80% wate) at a rate no faster than 3mL/min.

⑥ Measure the volume of colleted eluate from the SPE column.

⑦ Filte ⑥ with a 0.5 μm or smaller PTFE syringe filter for the analysis in the HPLC.

Instrument Conditions & Chromatogram

1. Extraction (Solid phase extraction, Liquid/liquid extraction)

YL9100Plus HPLC				
Solvents	A : Acetonitrile B : Water			
Column	C18 (4.6 mm x 250 mm x 5 µm)			
Flow rate	1.0-1.5 mL/min			
Temperature	30°C			
Injection volume	20 µL			
Detection	PDA, Dual wavelength(220nm, 274nm)			
Gradient programs	Time (min)	% A (ACN)	% B (Water)	Flow rate (mL/min)
	Initial	20	80	1.0
	7.3	20	80	1.0
	7.5	100	0	1.25
	8.0	100	0	1.5
	14.0	100	0	1.5
	23.0	20	80	1.0
	28.0	20	80	1.0

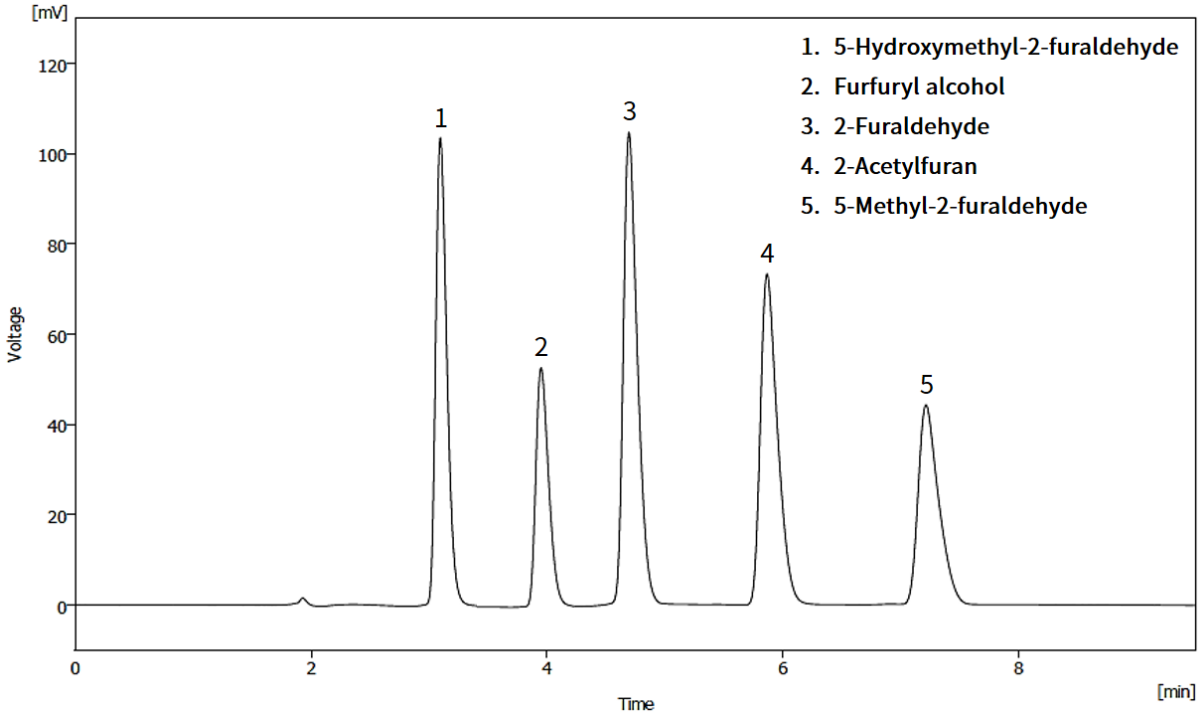

Figure 1. Furanic compounds chromatogram – Solid phase extraction

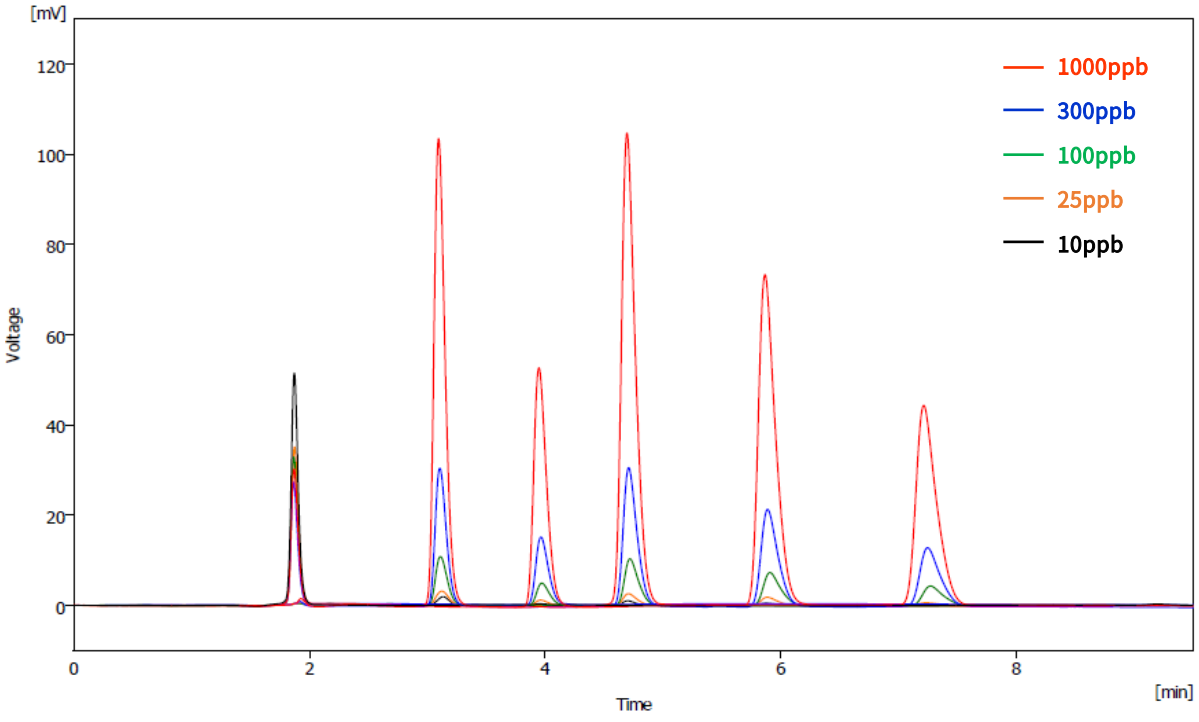

Figure 2. Overlay of furanic compounds chromatogram - Solid phase extraction

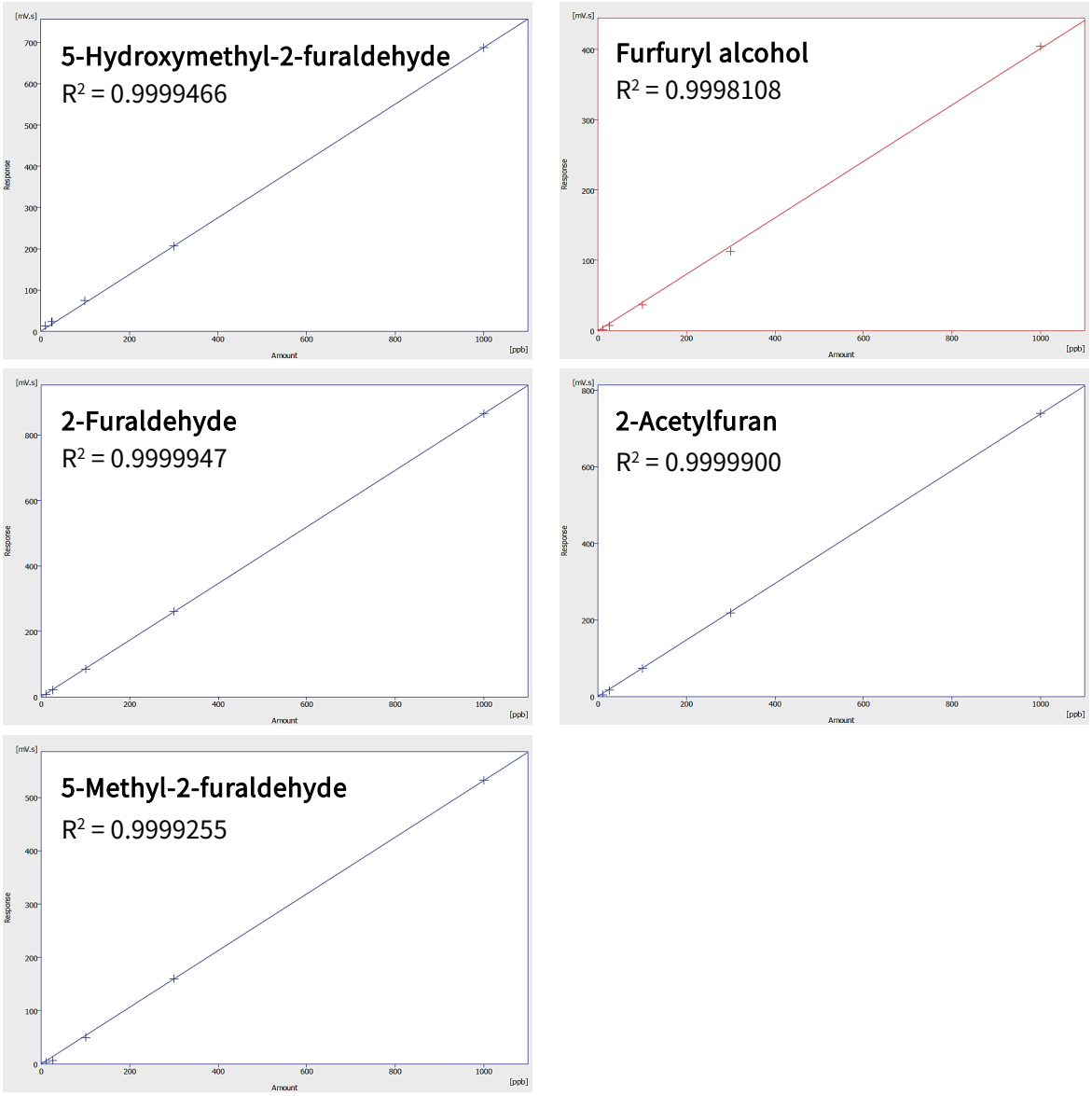

Figure 3. Calibration curves for furanic compounds – Solid phase extraction

Table 2. Validity of Test Method – Solid Phase Extraction (Concentration of 100 µg/kg)

	Analyte	R.T. (min)	MDL (ppb)	Extraction efficiency (%)	Precision (%)	Precision (%) (ASTM D5837기준)
1	5-Hydroxymethyl-2-furaldehyde	3.10	1.40	98.7	0.50	5.5
2	Furfuryl alcohol	3.95	3.98	96.9	1.40	16.7
3	2-Furaldehyde	4.70	1.64	97.8	0.58	6.0
4	2-Acetylfuran	5.87	2.22	91.0	0.78	7.7
5	5-Methyl-2-furaldehyde	7.21	3.67	96.2	1.29	6.0

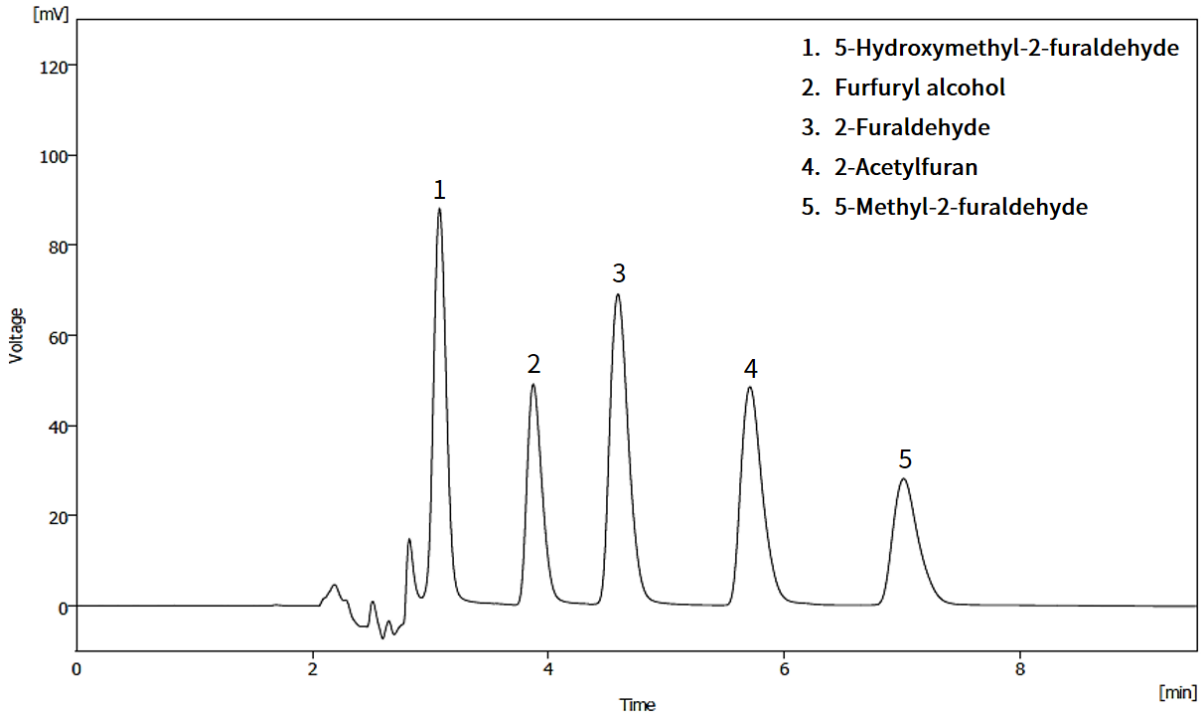

Figure 4. Furanic compounds chromatogram – Liquid/liquid exraction

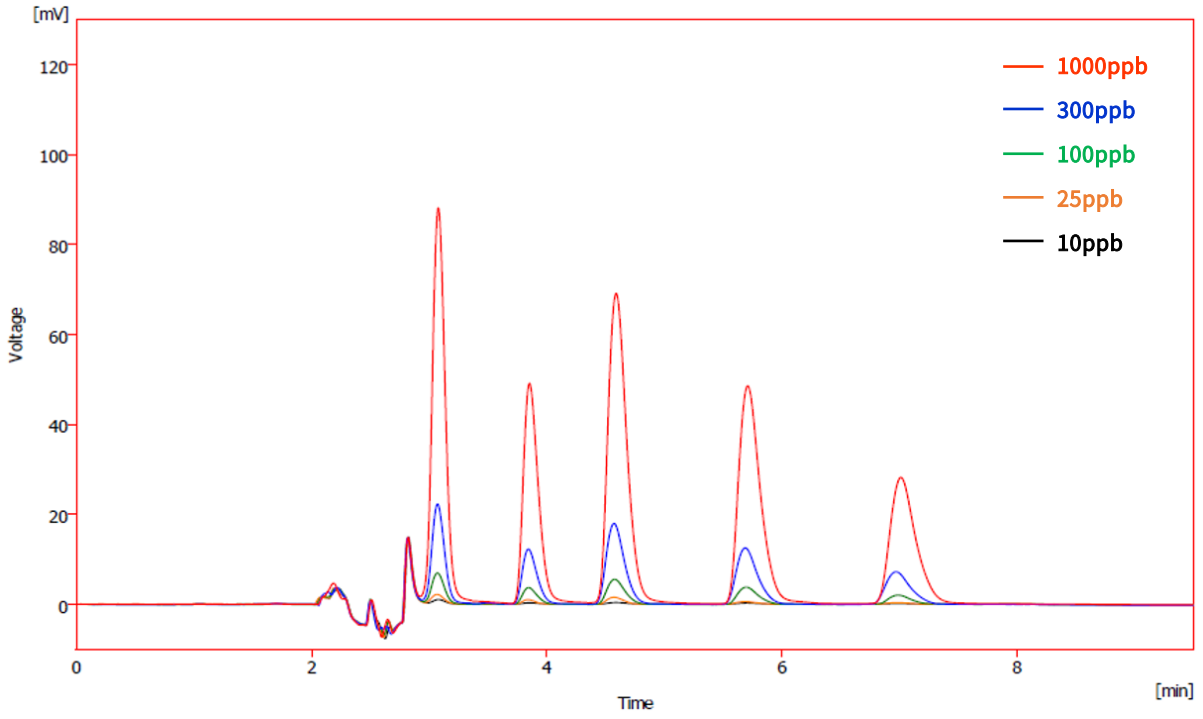

Figure 5. Overlay of furanic compounds chromatogram – Liquid/liquid exraction

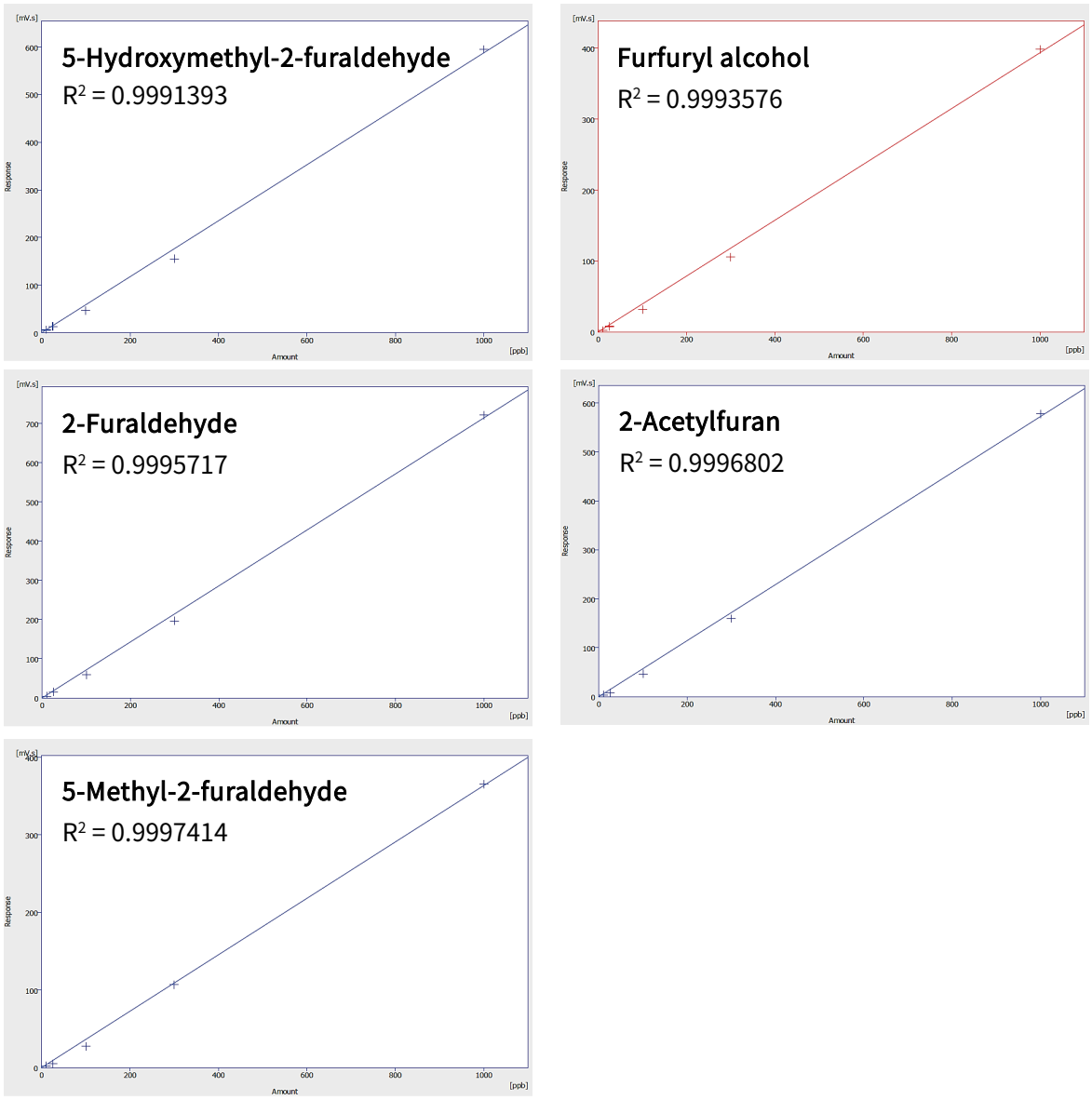

Figure 6. Calibration curves for furanic compounds – Liquid/liquid extraction

Table 3. Validity of Test Method – Liquid/liquid Extraction (Concentration of 100 µg/kg)

	Analyte	R.T. (min)	MDL (ppb)	Extraction efficiency (%)	Precision (%)	Precision (%) (ASTM D5837기준)
1	5-Hydroxymethyl-2-furaldehyde	3.07	1.74	87.1	0.62	11.7
2	Furfuryl alcohol	3.87	1.96	81.2	0.69	5.2
3	2-Furaldehyde	4.57	6.07	72.7	2.17	8.0
4	2-Acetylfuran	5.69	3.73	69.9	1.31	5.5
5	5-Methyl-2-furaldehyde	6.99	3.58	71.4	1.29	3.3

2. Direct Injection

YL9100Plus HPLC				
Solvents	A : Acetonitrile B : Water			
Column	C18 (4.6 mm x 250 mm x 5 µm)			
Flow rate	1.0-3.5 mL/min			
Temperature	30°C			
Injection volume	30 µL			
Detection	PDA, 274nm			
Gradient programs	Time (min)	% A (ACN)	% B (Water)	Flow rate (mL/min)
	Initial	20	80	1.0
	3.0	50	50	1.0
	5.3	50	50	1.5
	7.0	100	0	2.0
	9.0	100	0	3.0
	10.0	100	0	3.5
	18.8	100	0	2.0
	20.0	50	50	2.0
	22.0	20	80	2.0
	25.0	20	80	1.0

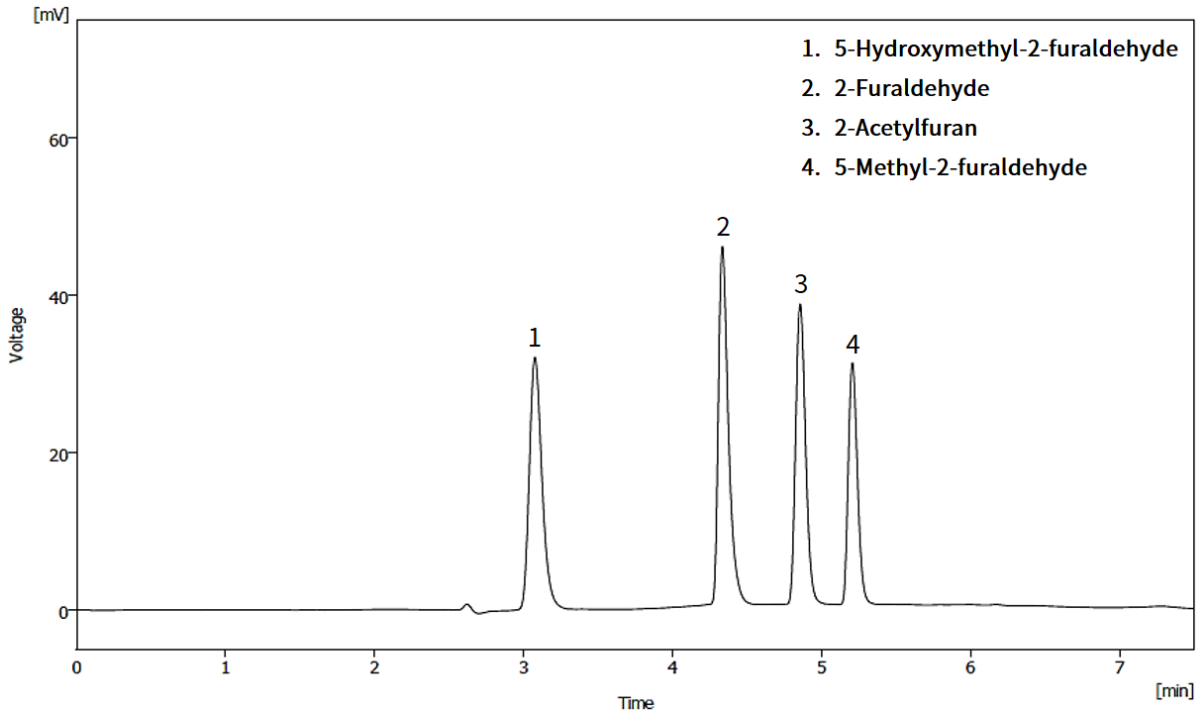

Figure 7. Furanic compounds chromatogram – Direct injection

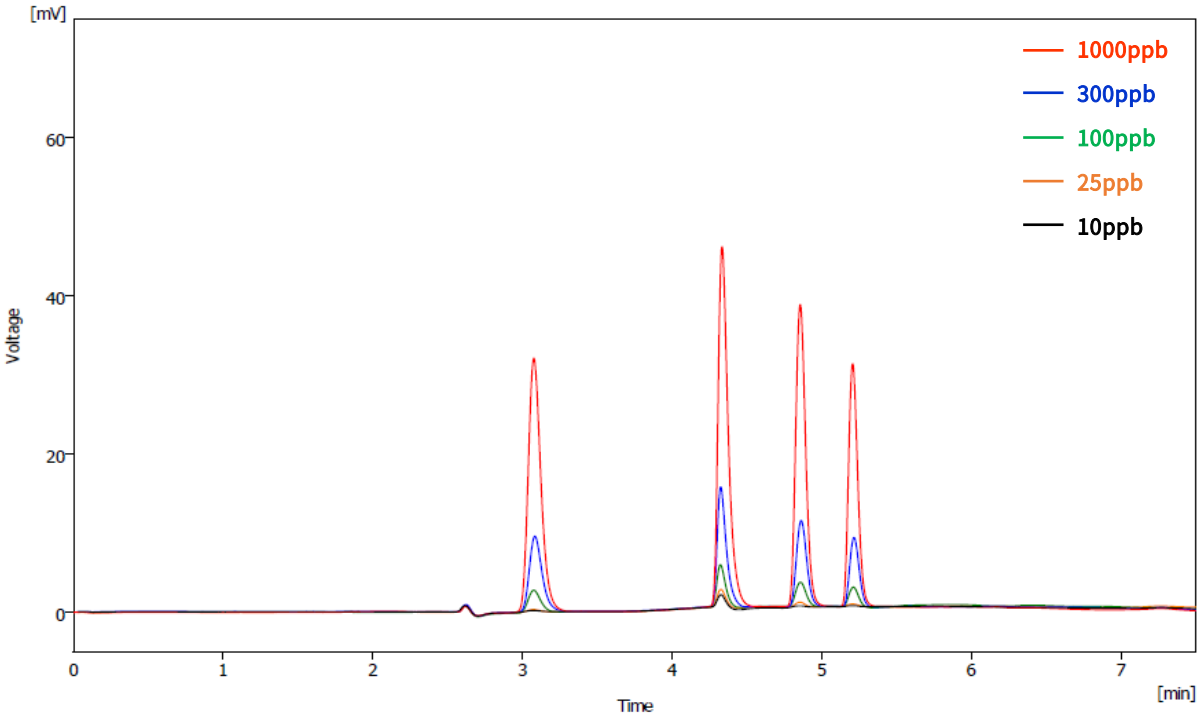

Figure 8. Overlay of furanic compounds chromatogram – Direct injection

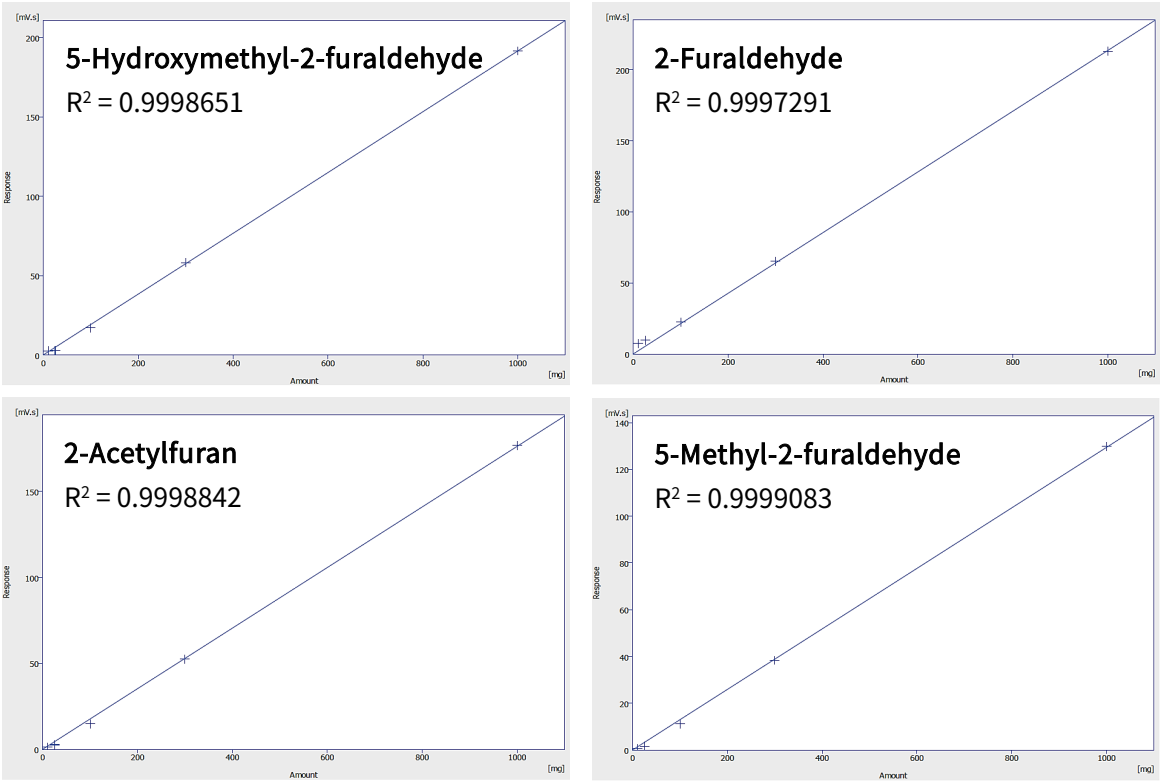

Figure 9. Calibration curves for furanic compounds - Direct injection

Table 4. Validity of Test Method – Direct Injection (Concentration of 100 µg/kg)

	Analyte	R.T. (min)	MDL (ppb)	Precision (%)	Precision (%) (ASTM D5837기준)
1	5-Hydroxymethyl-2-furaldehyde	3.05	9.46	3.35	4.9
2	2-Furaldehyde	4.29	10.67	3.73	10.6
3	2-Acetylfuran	4.83	23.23	7.75	12.6
4	5-Methyl-2-furaldehyde	5.18	13.85	5.21	6.0

Calculation

$$C_T = (R_T/R_S) \times C_S \times (V_T/V_E)$$

C_T = Concentration of furanic copound in the sample

R_T = Integrated peak area for furanic compound in the sample

R_S = Integrated peak area for furanic compound in daily calibration standard in oil

C_S = Concentration of furanic compound in daily calibration standard in oil

V_E = Volume of extraction solvent used to extract the calibration standard in oil

V_T = Volume of extraction solvent used to extract the sample

Extraction Efficiencies

To determine the extraction efficiency for each furanic compounds, run 1 mg/L의 extraction standards in solvent and 1 mg/L의 calibration standards in oil three times each. The averate peak area for each compound is used to calculate the extraction efficiency from the appropriate equation as follows.

Liquid/liquid extraction : $EE, \% = (R_O/R_S) \times (V_E/10) \times D_f \times 100$

Solid-phase extraction : $EE, \% = (R_O/R_S) \times (V_E/10) \times 100$

$EE =$ Extraction efficiency

$R_O =$ Average peak area of calibration standard in oil 1 mg/L

$R_S =$ Average peak area of extraction standard in solvent 1 mg/L

$V_E =$ Volume of solvent used for extraction

$10 =$ Constant (Volume of oil standard used for analysis is 10 mL)

$D_f =$ Dilution factor for Liquid/liquid extraction. (D_f=1, if there is no dilution of the extract)

Conclusion

The linearity, accuracy, precision (RSD %) and method detection limit (MDL) were evaluated to verify the validity of analysis results for each analysis method.

([Fig 3] & [Table 2] for Solid phase extraction/ [Fig 6] & [Table 3] for Liquid/liquid extraction/ [Fig 9] & [Table 4] for Direct injection)

The precision is calculated by 10 sequence injections according to ASTM D5837 and the method detection limit (MDL) is referred by Environment Research QA/QC Handbook by National Institute of Environmental Research (2011).

In this study, 5 kinds of furanic compounds were analyzed by YL9100 Plus HPLC/PDA according to ASTM D5837 method.

Among these 3 type of methods (Solid phase extraction, Liquid/liquid extraction, Direct injection), the solid phase extraction has the highest sensitivity with the superior extraction efficiency and the great peak shape but it requires a SPE column use and the preparation takes long due to the complicated extraction procedure. The liquid/liquid extraction provides a simpler extraction procedure that SPE but the extraction efficiency and precision is relatively lower. The direct injection, the simpliest method among all of these 3 methods, has a higher limit of detection, especially for furfuryl alcohol with low sensitivity because there is an unstable baseline with drift and a poor precision due to a matrix effect at 220nm (where furfuryl alcohol is best measured).

The correlation coefficients of calibration curve for furanic compounds in all 3 types of methods was determined to greater than 0.999 and the precision is also better than the ASTM D5387 regulation. As the result, YL9100 Plus HPLC satisfies with ASTM D5837 regulation and verifies reliable data in any of indicated 3 preparation methods.

Reference

- ASTM D 5837-99 (Reapproved 2005) Standard Test Method for Furanic Compounds in Electrical Insulating Liquids by High Performance Liquid Chromatography (HPLC)

-Environment Research QA/QC Handbook_ National Institute of Environmental Research (2011)

- Korea Electric Power Corporation Electric Power Research Institute; the dissolved gas in oil criteria of vegetable oil immersed power transformer

- Korea Electric Power Corporation Electric Power Research Institute; Simple Test Method for Furan in Aged Transformer Oil and its Kit

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