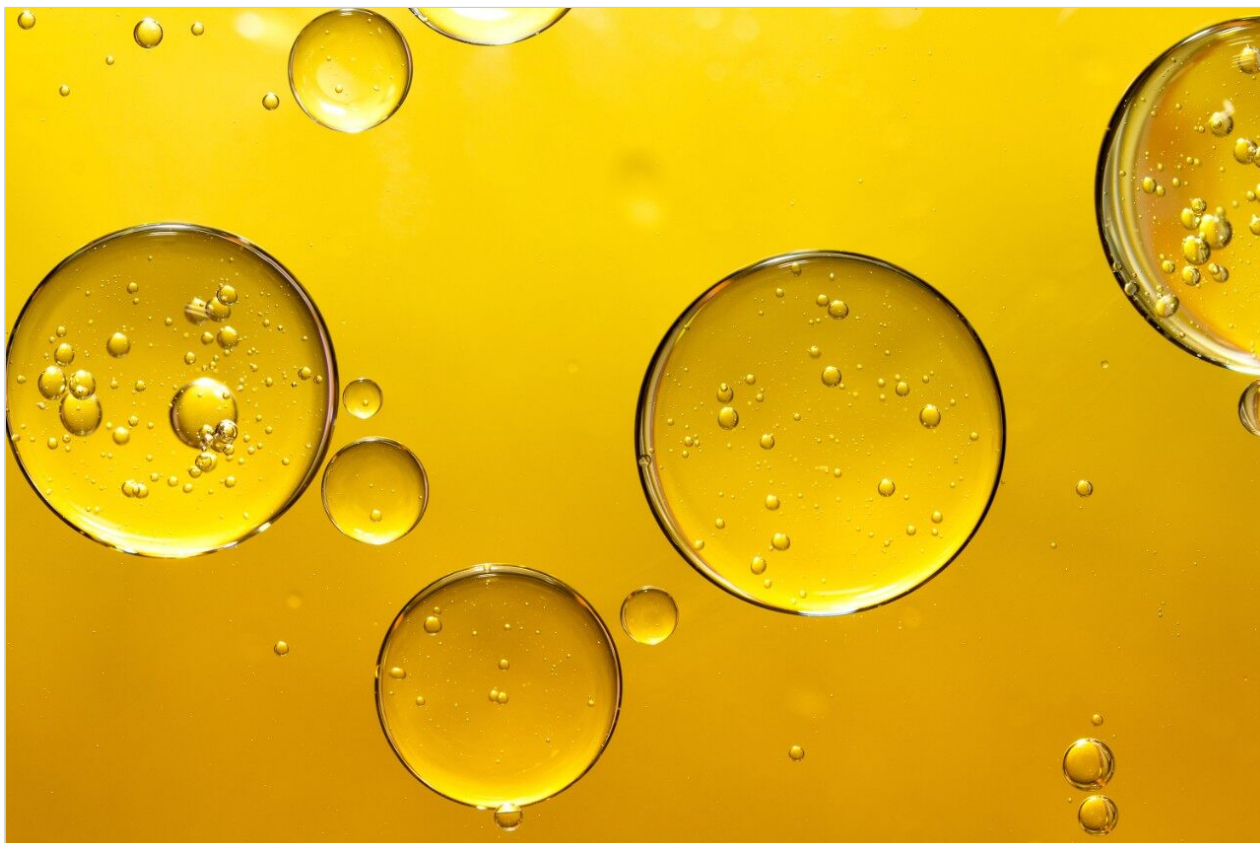# Waters™

Improving the Speed and Quantitative Performance for the Separation of Furans and the Passivator Benzotriazole in Transformer Oil Analysis

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Abstract

Two fast, selective, and sensitive methods have been developed for the analysis of furans and the passivator benzotriazole in transformer oil. One method utilizes the ACQUITY UPLC H-Class System coupled to the ACQUITY UPLC PDA Detector for the rapid four-minute analysis of furans alone. The second method utilizes the ACQUITY UPLC H-Class System coupled to Xevo TQ MS if furans and additional transformer oil additives are required, the passivator benzotriazole was considered within this application.

Benefits

This application note illustrates increased sample throughput for the identification and quantification of furans and the passivator benzotriazole in transformer oil offering:

- Reduction of solvent usage due to reduced run times.

- Improved sensitivity, selectivity, and robustness, compared with existing methodologies.

Introduction

Transformer oil is usually a highly-refined mineral oil and due to its stability at high temperatures, it has excellent electrical insulating and heat transfer properties. Because of these properties transformer oil has many uses including: oil-filled transformers, high-voltage capacitors, fluorescent lamp ballasts, high-voltage switches, and in circuit breakers.

Furanic compounds can originate from the thermal depolymerization of cellulose solid insulation used within electrical equipment, which can then migrate into the transformer oil.

Electrical and mechanical stresses and the presence of water and oxygen increase the degree of cellulose degradation, eventually rendering the transformer ineffective. These changes can occur either due to normal aging or the presence of a fault.

Therefore an effective preventative maintenance program is critical to aid the planning of system servicing and, as a result, reduce costly instrument downtime. Periodic analysis of transformer oil for furans can be used to assess the degree of depolymerization of the cellulose, which does not require taking the unit out of service in order to take a sample.

Various additives can be incorporated into transformer oil to boost the quality of the oil, for either short or long term. All additives present need to be declared, therefore methodology to confirm the presence of

declared additives, for example the passivator benzotriazole (BTA) – but also to detect undeclared additives, for example passivator Irgamet 30[1] – could be very valuable.

The presence of corrosive sulfur in transformer oil could potentially cause expensive power transformer failures. Passivators[2] (metal deactivators), such as BTA, act as long term corrosion inhibitors when added to transformer oil. They react with reactive metal surfaces both on metal surfaces and with dissolved metals (copper and silver) therefore reducing the rate of reaction with other compounds in the oil such as corrosive sulfur. But there are passivators, for example Irgamet 30,[1] that are not declared but are added to transformer oils to temporarily boost the oils quality to aid the passing of acceptance testing, therefore giving a false indication about the quality of the transformer oil.

Experimental

Sample preparation

Transformer oil analysis

- 1-mL transformer oil was extracted with 2 mL of acetonitrile for 1 min using a vortex mixer.
- 100 µL of the acetonitrile layer were transferred to an LC vial and diluted with 900 µL water.

LC conditions

LC system:	ACQUITY UPLC H-Class
Runtime:	4.00 min
Column:	ACQUITY UPLC BEH C_{18} 1.7 µm, 2.1 x 150 mm
Column temp.:	40 °C
Sample temp.:	10 °C
Mobile phase A:	Water:(0.1% formic acid)
Mobile phase B:	Acetonitrile:(0.1% formic acid)

	Flow rate:	0.45 mL/min

Flow rate: 0.45 mL/min

Injection volume: 10.0 µL

Mobile phase gradient is detailed in Table 1.

	Time (min)	Flow rate (mL/min)	%A	%B	Curve
1	Initial	0.450	80	20	–
2	1.50	0.450	80	20	6
3	2.00	0.450	60	40	6
4	2.01	0.450	0	100	6
5	3.00	0.450	0	100	6
6	3.01	0.450	80	20	6
7	4.00	0.450	80	20	6

Table 1. ACQUITY UPLC H-Class mobile phase gradient.

UV conditions (for furans)

UV system: ACQUITY UPLC PDA Detector

Range: 190 to 350 nm

Resolution: 1.2 nm

Sampling rate: 20 pts/sec

Filter time constant: Normal

MS conditions (for furans and the passivator benzotriazole)

MS system: Xevo TQ MS

Ionization mode: APCI positive

Corona current:	20 µA
Source temp.:	150 °C
APCI probe temp.:	400 °C
Desolvation gas:	1000 L/hr
Cone gas:	100 L/hr
Acquisition:	Multiple Reaction Monitoring (MRM)

Optimum UV absorbances were established for each furan, detailed in Table 2, for the analysis of furans.

Chemical substance		CAS number	Retention time (min)	UV optimum absorbance (nm)
Furans				
5-Hydroxymethyl-2-furaldehyde	5H2F	67-47-0	1.02	284
Furfuryl alcohol	2FOL	98-00-0	1.28	216
2-Furaldehyde	2FAL	98-01-1	1.45	277
2-Furylmethylketone	2ACF	1192-62-7	1.77	274
5-Methyl-2-furaldehyde	5M2F	620-02-0	2.13	292

Table 2. Furans, associated CAS numbers, expected retention times, and the UV optimum absorbances.

The standard method for the analysis of furanic compounds in electrical insulating liquids is ASTM D5837-12,[3] which uses HPLC with UV detection. Other example methodologies for the analysis of furanic compounds include: UPLC with UV detection,[4] HPLC analysis using various detection methods including ultraviolet (UV),[5] mass spectrometry (MS),[6] refractive index,[5] spectrophotometric[7] analysis, and gas chromatography-mass spectrometry (GC-MS).

Many previously used methods for furans consider only one furan (2-furaldehyde[6]) and lack reproducibility, selectivity, and sensitivity: they also require lengthy, costly, and time-consuming pre-treatments (SPE, concentration stages).

This application note describes two methods for the analysis of furans and the passivator benzotriazole in transformer oil. One method utilizes Waters ACQUITY UPLC H-Class System coupled to an ACQUITY UPLC PDA Detector for the rapid four-minute analysis of furans alone. The second method utilizes Waters

ACQUITY UPLC H-Class System coupled to Xevo TQ MS if the passivator benzotriazole analysis is also required.

MS conditions were also optimized, detailed in Table 3, for the analysis of furans and the passivator benzotriazole. The established MRM method is illustrated in Figure 1.

Chemical substance		CAS Number	Retention time (min)	Cone voltage (V)	Transition	Collision energy
Furans						
5-Hydroxymethyl-2-furaldehyde	5H2F	67-47-0	1.05	20	127.0 › 109.0	15
					127.0 › 81.0	20
Furfuryl alcohol	2FOL	98-00-0	1.30	25	81.1 › 53.0	15
2-Furaldehyde	2FAL	98-01-1	1.46	25	97.1 › 69.0	15
					97.1 › 41.1	15
2-Furylmethylketone	2ACF	1192-62-7	1.79	20	111.1 › 43.0	20
					111.1 › 69.1	15
5-Methyl-2-furaldehyde	5M2F	620-02-0	2.15	25	111.1 › 55.0	20
					111.1 › 83.0	15
Passivator						
Benzotriazole	BTA	95-14-7	1.66	40	120.1 › 65.0	20
					120.1 › 92.0	20

Table 3. Furans and the passivator benzotriazole, associated CAS numbers, expected retention times, cone voltages, MRM transitions, and associated collision energy values.
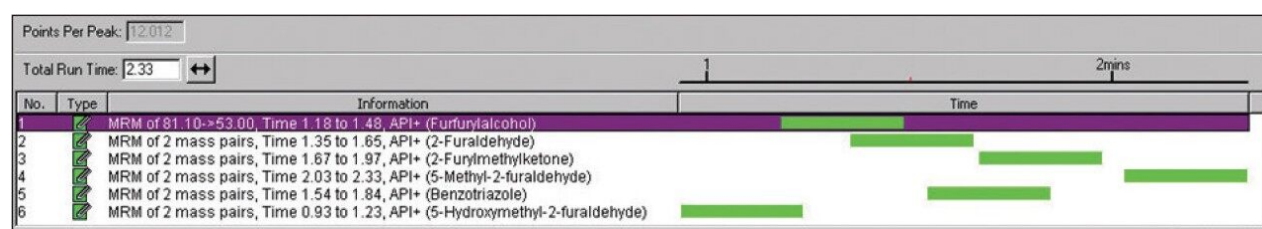

Figure 1. Furans MRM method (six compounds).

Instrument control, data acquisition, and result processing

Empower 3 Software was used for the UPLC-UV method.

MassLynx Software v.4.1 and TargetLynx Application Manager were used for the UPLC-MRM method.

Results and Discussion

Furans

The analysis of five furans was achieved using an ACQUITY UPLC H-Class System with an ACQUITY UPLC PDA Detector.

Optimum UPLC and UV conditions were developed, with the elution of all compounds within a four-minute run. When compared to the standard ASTM D5837-122 method with a minimum run time of 28 min, greater than seven times increase in sample throughput was achieved, with an excess of 88% less solvent usage.

Matrix matched mixed calibration standards, 0.01 to 5.00 µg/mL, were prepared and analyzed for all the compounds considered (equivalent range of 2 to 100 mg/kg in transformer oil using the developed method).

The calibration curve results generated by Empower Software for 5-hydroxymethyl-2-furaldehyde are shown in Figure 2, and the UV chromatograms, including associated UV spectra for each compound, are shown in Figure 3.

Method 12th june furans 292_3 Date/Time 6/13/2012 4:44:07 PM BST

System Channel 292.3nm

Component 5-Methyl-2-furaldehyde Time (min) 2.130

Equation $Y = -8.09e+002\,X^2 + 1.99e+005\,X + 2.75e+002$

R^2 0.999964 R 0.999982 Standard Error 3.790057e+002

RSS 7.182266e+005 RSD 453.392210 Weighting 1/X

Codes

RSD(E) 3.217958

Norm Intercept/Slope

Calibration

Level	X Value	Response	Calc. Value	% Deviation
1	0.01	2147	0.009	-5.81
2	0.05	10404	0.051	1.93
3	0.10	20566	0.102	2.11
4	0.25	51139	0.256	2.45
5	0.50	99573	0.501	0.10
6	1.00	197289	0.995	-0.50
7	2.50	490332	2.490	-0.39
8	5.00	975123	5.006	0.11

Individual Points Average Points

For Help, press F1

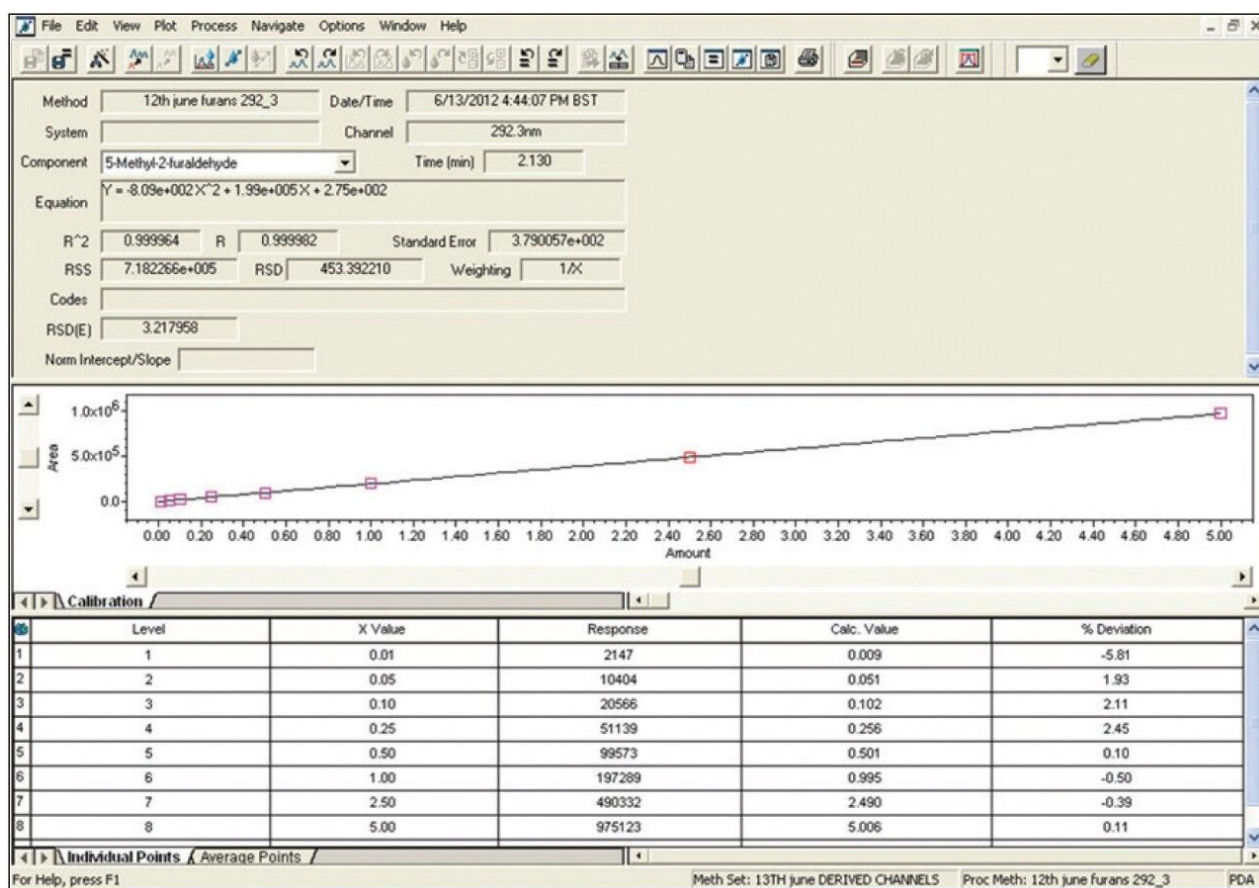Meth Set: 13TH june DERIVED CHANNELS Proc Meth: 12th june furans 292_3 PDA

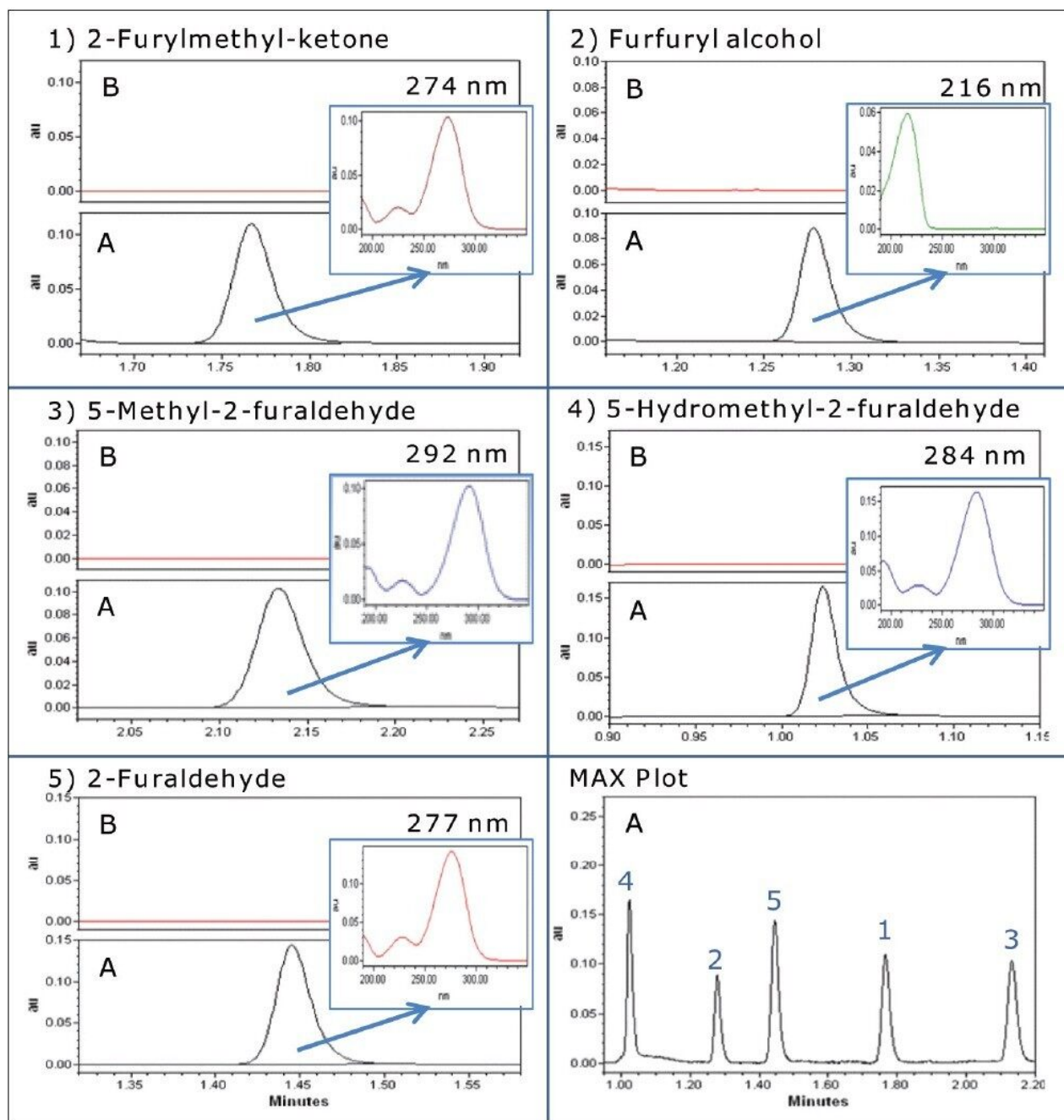*Figure 2. Empower Software calibration curve for 5-hydroxymethyl-2 furaldehyde.*

Figure 3. UV chromatograms and associated UV spectra for each furan in A) a mixed matrix matched 1 µg/mL calibration standard (equivalent to 20 mg/kg in transformer oil), and B) blank transformer oil.

Transformer oil analysis

Using the transformer oil analysis extraction and instrument parameters as detailed, the furan results obtained for the analysis of spiked transformer oil are detailed in Table 4. Recoveries were obtained by comparing extracted spiked transformer oil against matrix matched calibration standards.

Compound		UV results		
		Replicate injection results (mg/kg)		Average recovery (%)
		1	2	
5-Hydroxymethyl-2-furaldehyde	Blank	ND	–	–
	2 mg/kg	1.63	1.64	81.9
	10 mg/kg	9.37	9.36	93.6
Furfuryl alcohol	Blank	ND	–	–
	2 mg/kg	1.89	1.87	93.8
	10 mg/kg	9.51	9.38	94.5
2-Furaldehyde	Blank	ND	–	–
	2 mg/kg	1.90	1.91	95.1
	10 mg/kg	9.54	9.55	95.4
2-Furylmethylketone	Blank	ND	–	–
	2 mg/kg	1.94	1.95	97.3
	10 mg/kg	9.59	9.58	95.8
5-Methyl-2-furaldehyde	Blank	ND	–	–
	2 mg/kg	1.86	1.86	93.2
	10 mg/kg	9.96	10.01	99.8

Table 4. Transformer oil spiked with furans recovery data. Results obtained using PDA detection and quantified against matrix matched mixed calibration standards. ND = not detected.

Efficient recoveries were obtained, ranging between 82% to 100% for two replicates, no evidence of matrix interference was observed.

Furans and the passivator benzotriazole

The analysis of six compounds (five furans and the passivator benzotriazole) was achieved using Waters Xevo TQ MS in MRM mode with APCI ionization, coupled to an ACQUITY UPLC H-Class System.

Optimum UPLC and MRM conditions were developed, with the elution of all compounds within a four-minute run.

Transformer oil analysis

The MRM mass detection method detailed in Figure 1 was used after appropriate sample preparation to quantify for furans in transformer oil (containing furans and the passivator benzotriazole).

Using the transformer oil analysis extraction and instrument parameters as detailed, the furan results obtained for the analysis of spiked transformer oil are detailed in Table 5. Recoveries were obtained by comparing extracted spiked transformer oil against matrix matched calibration standards.

Compound		MS results		
		Replicate injection results (mg/kg)		Average recovery (%)
		1	2	
Benzotriazole	Blank	ND	–	–
	2 mg/kg	1.97	1.95	98.1
	10 mg/kg	10.55	10.27	104.1
5-Hydroxymethyl-2-furaldehyde	Blank	ND	–	–
	2 mg/kg	1.97	1.95	95.0
	10 mg/kg	10.55	10.27	95.4
Furfuryl alcohol	Blank	ND	–	–
	2 mg/kg	1.71	1.64	83.6
	10 mg/kg	10.41	10.01	102.1
2-Furaldehyde	Blank	ND	–	–
	2 mg/kg	1.73	1.93	91.5
	10 mg/kg	9.11	8.49	88.0
2-Furylmethylketone	Blank	ND	–	–
	2 mg/kg	1.74	1.75	87.4
	10 mg/kg	9.90	10.10	100.0
5-Methyl-2-furaldehyde	Blank	ND	–	–
	2 mg/kg	1.99	2.09	102.0
	10 mg/kg	10.56	10.58	105.7

Table 5. Transformer oil spiked with furans recovery data. Results obtained using mass spectrometric detection and quantified against matrix matched mixed calibration standards. ND = not detected.

Efficient recoveries were obtained, ranging between 84% to 105% for the two replicates. Additional benefits include improved selectivity and sensitivity for the analysis of furans and transformer oil additives (the passivator benzotriazole was considered within this application) using the Waters Xevo TQ MS in MRM mode.

Matrix matched mixed calibration standards, 0.01 to 5.00 µg/mL, were prepared and analyzed for all the compounds considered (equivalent range of 2 to 100 mg/kg in transformer oil using the developed method). The TargetLynx Quantify results for 5-hydroxymethyl-2-furaldehyde are shown in Figure 4, and the MRM chromatograms for each compound are shown in Figure 5.

#	Name	Sample Text	Type	Std. Conc	RT	Conc.	Area	S/N
2	2	furans_29th May_028	5 ppm mixed furan standard in matrix	Standard	5.0000	1.04	4.99935	83200	2489819
3	3	furans_29th May_029	2.5 ppm mixed furan standard in matrix	Standard	2.5000	1.04	2.50324	43300	1310363
4	4	furans_29th May_030	1.0 ppm mixed furan standard in matrix	Standard	1.0000	1.05	0.99455	17600	525905
5	5	furans_29th May_031	0.5 ppm mixed furan standard in matrix	Standard	0.5000	1.05	0.49932	8920	261661
6	6	furans_29th May_032	0.25 ppm mixed furan standard in matrix	Standard	0.2500	1.05	0.25401	4560	133131
7	7	furans_29th May_033	0.1 ppm mixed furan standard in matrix	Standard	0.1000	1.05	0.09778	1760	52031
8	8	furans_29th May_034	0.05 ppm mixed furan standard in matrix	Standard	0.0500	1.05	0.05203	938	27827
9	9	furans_29th May_035	0.01 ppm mixed furan standard in matrix	Standard	0.0100	1.05	0.00971	178	5326
10	10	furans_29th May_036	blk (matrix)			1.06		2.96	74

Calibration: 12 Jun 2012 11:21:09

Compound name: 5-Hydroxymethyl-2-furaldehyde
Coefficient of Determination: R^2 = 0.999971
Calibration curve: -269.869 * x^2 + 17991.2 * x + 3.00375
Response type: External Std, Area
Curve type: 2nd Order, Origin: Exclude, Weighting: 1/x, Axis trans: None

Chromatogram

furans_29th May_031 Smooth(SG,2x2)   F6:MRM of 2 channels,API+
0.5 ppm mixed furan standard in matrix   127 > 109
5-Hydroxymethyl-2-furaldehyde;1.05;261661   2.622e+005

furans_29th May_031 Smooth(SG,2x2)   F6:MRM of 2 channels,API+
0.5 ppm mixed furan standard in matrix   127 > 81
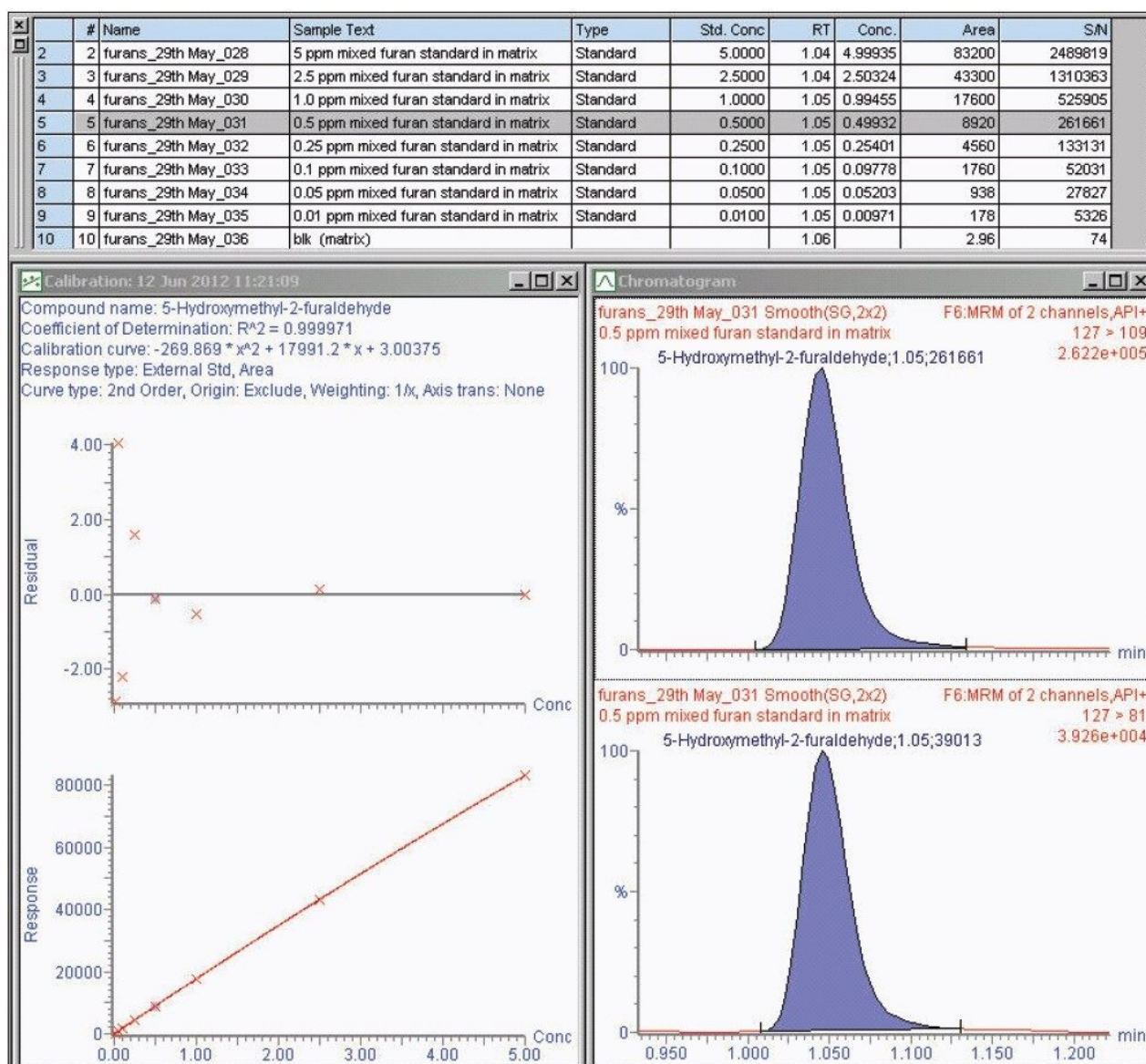5-Hydroxymethyl-2-furaldehyde;1.05;39013   3.926e+004

Figure 4. TargetLynx Quantify results browser shows the calibration quantitation results, calibration curve, and example MRM chromatogram for 5-hydroxymethyl-2-furaldehyde.
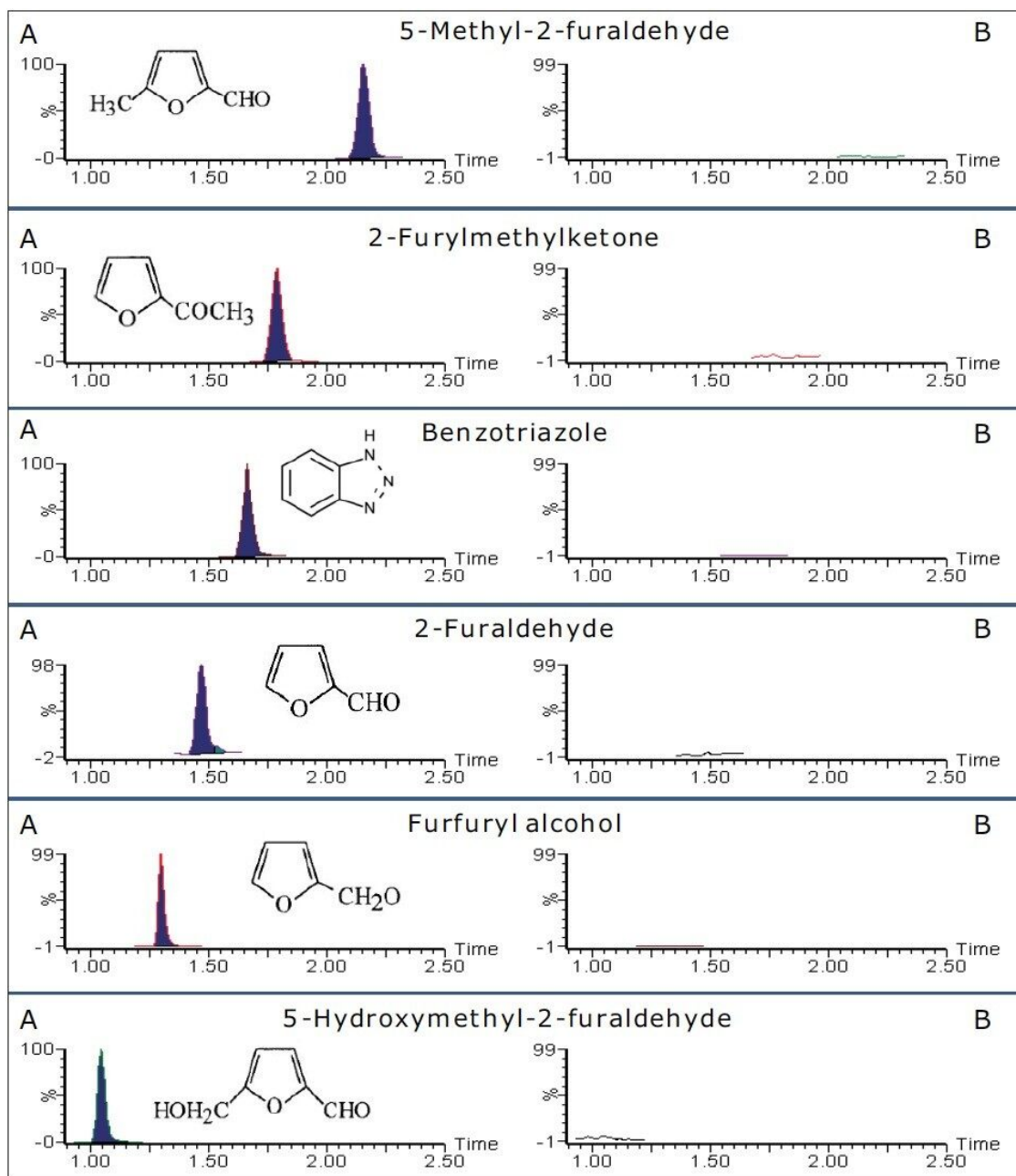
Figure 5. MRM chromatograms for furans and the passivator benzotriazole in A) a mixed matrix matched 1 μg/mL calibration standard (equivalent to 20 mg/kg in transformer oil), and B) blank transformer oil.

Conclusion

Two fast, selective, and sensitive methods have been developed for the analysis of furans and the passivator benzotriazole in transformer oil.

One method utilizes the ACQUITY UPLC H-Class System coupled to the ACQUITY UPLC PDA Detector for the rapid four-minute analysis of furans alone. The second method utilizes the ACQUITY UPLC H-Class System coupled to Xevo TQ MS if furans and additional transformer oil additives are required, the passivator benzotriazole was considered within this application.

The described approach offers many benefits when compared to the standard method:

- Business benefits of using UPLC analysis including, greater than seven times increase in sample throughput and an excess of 88% less solvent usage.
- Enhanced sensitivity and selectivity resulting in improved confidence in identification and quantification offered using Xevo TQ MS.

APCI provides an efficient ionization mode for the analysis of the broad distribution of diverse polarities of the compounds being analyzed.

Quantitative furan analysis as detailed, using a small amount of insulating oil sampled from the transformer (without taking it out of operation), can be used as a representation of the degree of depolymerization and hence establish the condition of the transformer.

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