



## SIMULTANEOUS MEASUREMENT OF WATER, METHANOL AND TOTAL GLYCERIN IN BIODIESEL SYNTHETIC SAMPLES USING A MC2750 EP-NIR SPECTROMETER.

**SUMMARY:** An Aspectrics MC2750 EP-NIR spectrometer equipped with a dip probe (2-mm pathlength) was used to develop a calibration for the measurement of the water, methanol and total glycerin in B100 biodiesel. This study proves this non-destructive rapid measurement method to be very accurate (95% accuracy of  $\pm 0.011\%$ ;  $\pm 0.017\%$  and  $\pm 0.029\%$ ) for the measurement of water, methanol and total glycerin, respectively. A comparison of analytical performance to regulatory requirements and an estimate of R.O.I. for biodiesel producers regulatory compliance is also proposed.

### SCOPE OF STUDY

Biodiesel results from the alkali methyl-esterification of free fatty acids hydrolyzed from mono-, di- and tri-glycerides of various sources.

US <sup>(1)</sup> and European <sup>(2)</sup> define precisely the maximum levels of contamination allowed in B100 (pure) biodiesel finished product. Of particular interest are the maximum allowable concentrations of water (natural contaminant), methanol (reactant of the methyl esterification) and total glycerin (product of the MG, DG, TG hydrolysis) in the finished product.

B100 pure biodiesel must meet these requirements. Any batch not meeting these requirements can contaminate the entire supply chain with catastrophic economic consequences. Therefore, biodiesel producers must test their finished product (B100) to ensure they meet regulatory compositional requirements.

However, the cost of third party laboratory testing can significantly add to the cost of production of a single batch.

This study is designed to test the accuracy of a rapid, non-destructive method (EP-NIR spectrometry) for the simultaneous measurement of three of these B100 contaminants: water, methanol and total glycerin.

The goal of this applications note is to demonstrate that EP-NIR is a rapid and cost-effective means of screening biodiesel samples. Pre-screening the samples eliminates the costly number of non-compliant samples sent for third party analysis (approximate cost \$1200/sample).

### ANALYTICAL SUMMARY

Table 1. reports the accuracy and precision levels of the EP-NIR based method using three different algorithmic approaches. Biodiesel samples used to develop these methods were manufactured (synthetic samples) in order to achieve maximum variability of B100 composition with a minimum number of samples.

Using the best results, it can be reported that, if using an EP-NIR as a screening tool for B100 quality control, all the following samples can be exonerated from costly official method analysis:

- All sample with EP-NIR measured **water** contamination of 0.038% v/v or less (Max allowed: 0.050% v/v)
- All sample with EP-NIR measured **methanol** contamination of 0.184% v/v or less (Max allowed: 0.200% v/v)
- All sample with EP-NIR measured **total glycerin** contamination of 0.221% v/v or less (Max allowed: 0.250% v/v)

### EXPERIMENTAL

#### Spectrometer:

- EP-NIR MC2750 (spectral range: 1.375 - 2.750  $\mu\text{m}$ )
- NearIR high power halogen source
- Transmission dip probe with 2 mm pathlength (resulting in maximum absorptions of approximately 1.2 O.D., well within the dynamic range and linear instrumental response range of the spectrometer.)

#### Samples:

Synthetic samples were prepared from the following fractions:

- B100 (with 0.19% total glycerin, 0% methanol and 0% water)
- Methanol (collected at the B100 production site)
- Total glycerin (collected at the B100 production site)
- Distilled water.

Synthetic samples were prepared using an orthogonal experimental design to achieve maximum variability with minimum number of calibration standards.



Concentration ranges covered were:

- Water: 0.000 to 0.100 % v/v (maximum allowed by regulation: 0.050% v/v)
- Methanol: 0.10 to 0.30 % v/v (maximum allowed by regulation: 0.20% v/v)
- Total glycerin: 0.19 to 0.30 % w/w (maximum allowed by regulation: 0.25% w/w)

All samples were analyzed in 4 replicates.

#### Calibrations:

Calibration models using PLS1, PLS2 and PCR were developed using Grams AI 8.0.

In all cases, spectra pre-treatment consisted only of a mean centering and an automated 2-point baseline correction of all the absorbance spectra.

F-test statistical analysis was performed to identify outliers.

The graphing of Standard Error of Cross Validation as a function of the number of factors in the method and a PRESS analysis were used as criteria for the determination of the number of factors to include in each calibration model.

Statistical outputs used to qualify accuracy and precision of the methods were:

- Pearson Moment Correlation  $R^2$  (indicating of the quality of the fit of the calibration model)
- RMSEC (Root Mean of Standard Error of Calibration)
- Accuracy (95% confidence) defined as  $\pm 2 * RMSEC$
- Precision defined as the average of standard deviation of residual calculated concentrations for each set of 4 replicate results.

## RESULTS & DISCUSSION

#### Measurement of water in B100:

Best analytical results were obtained using the PCR algorithmic approach (Figure 2). Statistical outputs were  $R^2 = 97.86\%$ , RMSEC was 58 ppm (resulting in a 95% confidence accuracy in measurement of  $\pm 117$  ppm) and precision was 58 ppm.

#### Measurement of methanol in B100:

Best analytical results were obtained using the PLS1 algorithmic approach (Figure 3.) Statistical outputs were  $R^2 = 98.87\%$ , RMSEC was 95 ppm (resulting in a 95% confidence accuracy in measurement of  $\pm 189$  ppm) and precision was 91 ppm.

#### Measurement of glycerin in B100:

Best analytical results were obtained using the PLS1 algorithmic approach (Figure 4.) Statistical outputs were  $R^2 = 91.28\%$ , RMSEC was 145 ppm (resulting in a 95% confidence accuracy in measurement of  $\pm 290$  ppm) and precision was 144 ppm.

Overall, glycerin was the most difficult compound to model. The difficulty of the measurement can be better understood when looking at the chemical nature of the compound in relationship to the other molecules present in the matrix:

- **B100:** methyl ester of free fatty acids yielding IR absorption bands corresponding to  $-CH$  (alkyl) and  $R-COO-R'$  (ester) functional groups.
- **Water:** the  $-OH$  absorption characteristic (as shown by the water correlation spectrum in Figure 1) is very distinct from all other  $-OH$  functional group absorptions, making this measurement relatively easy.
- **Methanol:** the  $-OH$  absorption created by the hydroxyl group in methanol (as shown by the methanol correlation spectrum in Figure 1) is also very distinct from all other  $-OH$  functional group absorptions, also making this measurement relatively easy.
- **Total Glycerin:** total glycerin create absorption characteristics relevant of both  $-OH$  (hydroxyl) and  $-CH$  (alkyl) functional group. As shown by the methanol correlation spectrum in Figure 1, we observe that the glycerin absorptions characteristics are a significant spectral interferent to the absorption characteristics of methanol. Moreover, the  $-CH$  (alkyl) information pertaining to the glycerin alone is also heavily interfered with by the alkyl information of the methyl esters of free fatty acids (the B100 itself.)

The reality of the chemistry and resulting spectral interferences shows in the analytical results. Assuming that the precision of manufacture of the synthetic samples was constant (using volumetric and gravimetric methods), we observed that the least interfered chemicals (water) produced the most accurate results, whereas the most interfered chemical (glycerin) produced the least accurate results.



**R.O.I. FOR B100 PRODUCERS**

The strengths of the Aspectrics' EP-NIR for B100 quality control include: speed of analysis, non-destruction of sample, ease of use and low cost of ownership (elimination of chemical use and subsequent disposal.)

EP-NIR, as a screening technique, is not designed to replace the official analysis method. However, as screening technique, EP-NIR can deliver immediate results in a cost-effective manner to exonerate as many batches of B100 as possible from the requirement of costly and lengthy reference method analysis by third party laboratory.

The following data confirms that using an Aspectrics MultiComponent 2750 EP-NIR Analyzer as a screening tool, one can eliminate sending noncompliant samples out for costly third party testing.

CONTAMINANT: WATER	
Regulation	< 0.050 % v/v (500 ppm)
EP-NIR 95% accuracy	± 117 ppm
Reference Method Analysis Exoneration Level: All Samples With ...	... EP-NIR water < 383 ppm (0.038 % v/v)

CONTAMINANT: METHANOL	
Regulation	< 0.20 % v/v (2,000 ppm)
EP-NIR 95% accuracy	± 165 ppm
Reference Method Analysis Exoneration Level: All Samples With ...	... EP-NIR methanol < 1,835 ppm (0.184% v/v)

CONTAMINANT: TOTAL GLYCERIN	
Regulation	< 0.25 % w/w (2,500 ppm)
EP-NIR 95% accuracy	± 290 ppm
Reference Method Analysis Exoneration Level: All Samples With ...	... EP-NIR total glycerin < 2,210 ppm (0.221 % w/w)

**CONCLUSION**

This study proves that EP-NIR spectrometry is fit to produce accurate results for the simultaneous measurement of water, methanol and total glycerin in a B100 biodiesel sample.

Moreover, the levels of accuracy reached demonstrates that the EP-NIR spectrometer can be relied upon as an efficient B100 quality control tool, allowing one to quickly screen B100 sample batches.

Furthermore, from a chemometrics view point, it appears that the pre-processing of the absorbance spectra (mean centering and 2-point automated baseline correction) had much more impact on improving the accuracy and precision of the measurement than switching from one multivariate algorithmic approach to the other (PLS1, PLS2 and PCR).

**BIBLIOGRAPHY**

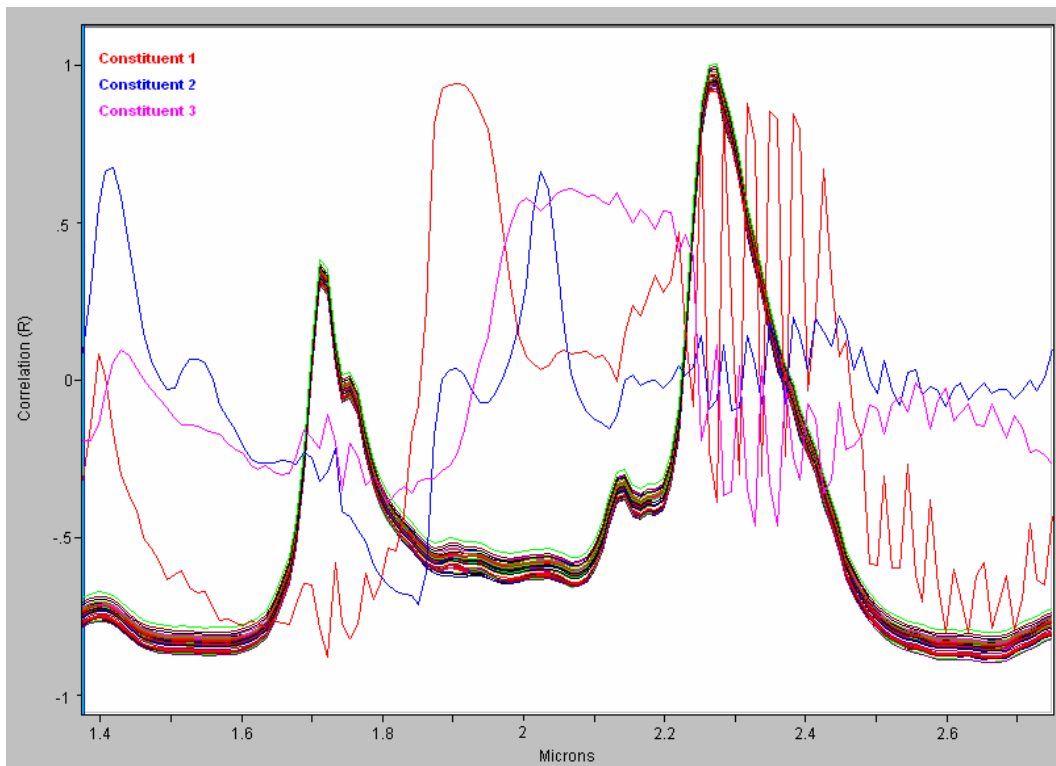
- (1) SPECIFICATION FOR BIODIESEL (B100) – ASTM D6751-06
- (2) Knothe, Gerhard. "Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters." Fuel Processing Technology 86 (2005) 1059– 1070.



**Table 1:** Summary of calibration results for the simultaneous measurement of water, methanol and total glycerin in biodiesel.

Comparison of algorithm performance (PLS1, PLS2, PCR) yields no significant advantage for any of the method, except for a slight disadvantage in using PLS2 method for the measurement of methanol in bio-diesel.

Chemical	Method	R <sup>2</sup>	RMSEC	95% Accuracy	Precision
Water	PLS1	0.9764	62 ppm	± 123 ppm	58 ppm
	PLS2	0.9727	95 ppm	± 189 ppm	91 ppm
	PCR	0.9786	58 ppm	± 117 ppm	58 ppm
Methanol	PLS1	0.9886	95 ppm	± 189 ppm	92 ppm
	PLS2	0.9887	95 ppm	± 189 ppm	91 ppm
	PCR	0.9914	83 ppm	± 165 ppm	83 ppm
Total Glycerin	PLS1	0.9128	145 ppm	± 290 ppm	144 ppm
	PLS2	0.9108	149 ppm	± 297 ppm	145 ppm
	PCR	0.9030	163 ppm	± 326 ppm	157 ppm



**Figure 1:** Spectra of the 55 calibration samples for the simultaneous measurement of water, methanol and glycerin in biodiesel.

In **Red**: correlation spectrum for **water** in biodiesel

In **Blue**: correlation spectrum for **methanol** in biodiesel

In **Pink**: correlation spectrum for **total glycerin** in biodiesel



### Water In Biodiesel - PCR

(Mixture Biodiesel + Water + Methanol + Glycerin)

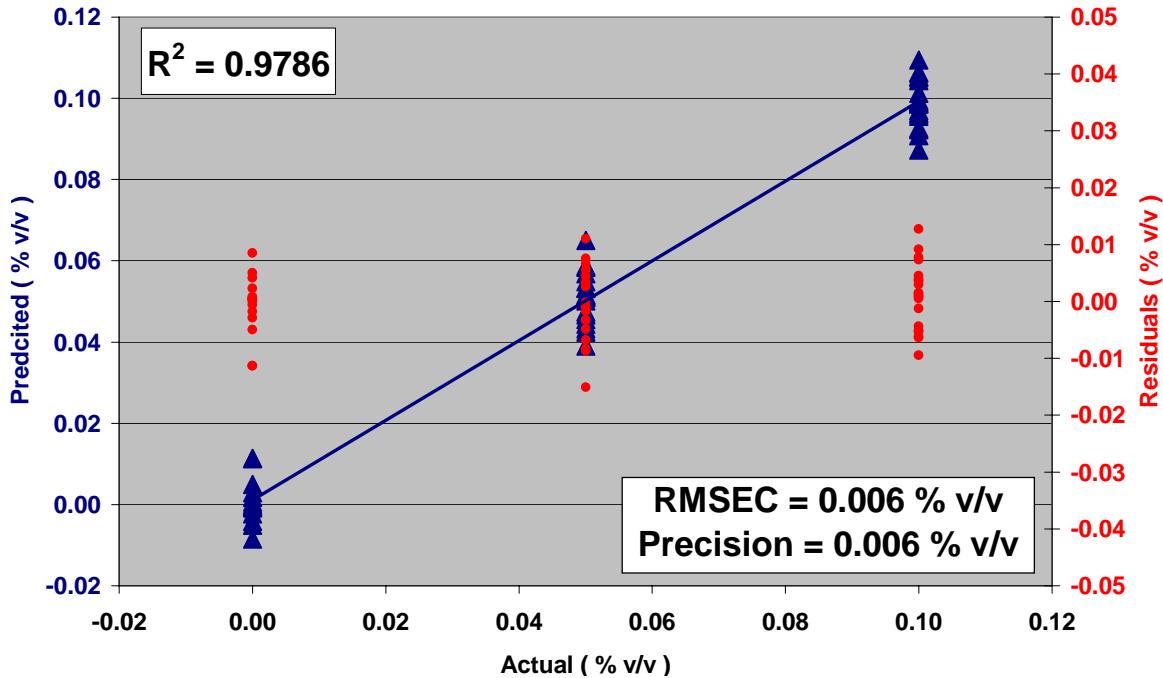


Figure 2:

Calibration results for water in biodiesel using PCR method.

### Methanol In Biodiesel - PLS1

(Mixture Biodiesel + Water + Methanol + Glycerin)

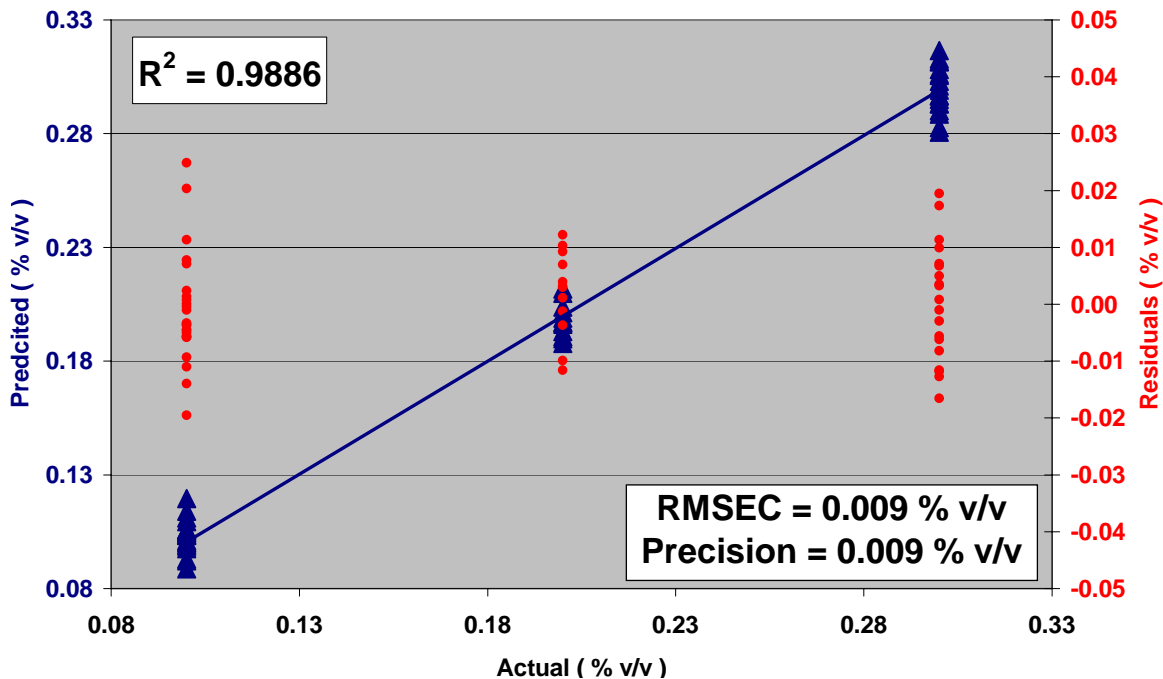


Figure 3:

Calibration results for methanol in biodiesel using PLS1 method.



### Glycerin In Biodiesel - PLS1

(Mixture Biodiesel + Water + Methanol + Glycerin)

