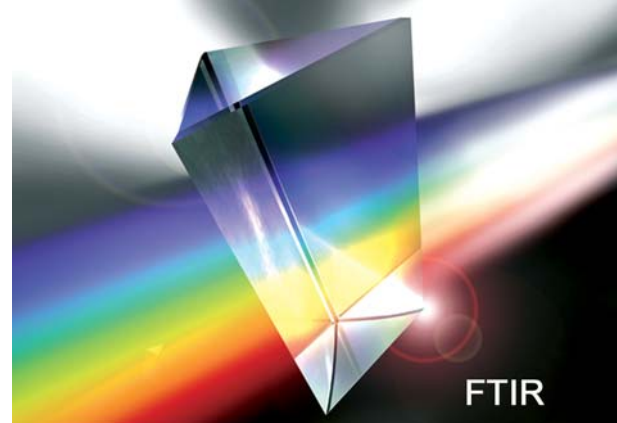


Application Note

Determination of Biodiesel blends based on rapeseed oil

FAME determination with single reflection ATR an alternative to DIN EN 14078



European agriculture produces a lot of plants containing oil which will be used for commercial purposes. For the food market the rapeseed oil is used as salad oil or as main part of margarine.

Actual the rapeseed oil is also a discussion point for the biodiesel aspects. Blends of the biodiesel are possible to be used for the standard motors of the cars with diesel engine. Most of the commercial motors are not able to run with the 100% of biodiesel. Blends of biodiesel are necessary.

The quality of such biofuel and the blends of it are controlled by the Biodiesel regulation. One aspect of the control is the FAME (Fatty acid methyl ester) contents which can be correlated direct to the blend level. The blend itself is the mixture of mineral oil and a biodiesel like rapeseed oil. A blend is declared as B5 and is 5% of biodiesel mixed into mineral oil by the means of volume v/v. Biodiesel like rapeseed oil is rich on fat molecules which are treated in a transesterification process to contain a variety of esters.

A method for the determination of FAME in a blend is shown in the DIN EN 14078. The method described is a wet chemical treatment to get best transmission mode spectra of standard solutions. The biodiesel blend is dissolved in this case in cyclohexane, this mixture is transferred into a liquid cell and measured by FTIR instrument technique.

In this paper is shown an alternative method using the oil in its natural appearance. Just a drop of oil or blend is placed on a crystal. This way of analysis is possible with the single reflection accessory or with the horizontal ATR. Both techniques are based

on attenuated horizontal reflection of the infrared beam through two media with different refractive index.

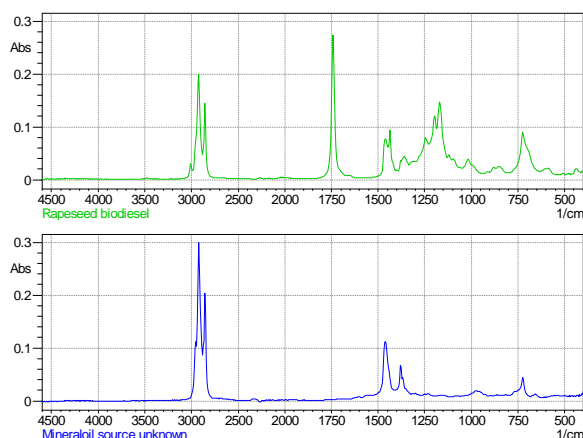


Fig. 1: Typical infrared absorbance spectra of pure mineral oil (blue) and a pure biodiesel (green), visible are the differences in region at 3007, 1750 and 1000 -1500 cm⁻¹

Sample preparation

Instead of the classical infrared transmission cell the single reflection technique was used for the measurements of the infrared spectra. One drop of the oil was placed on the measurement window, measured and later removed simply with a tissue and cleaning of remaining parts with a drop of solvent. System will be ready for measurement of next sample within one minute.

Calculation

To determine the contents of the FAME one possibility is to investigate into the PLS (Partial least square) quantitative modelling.

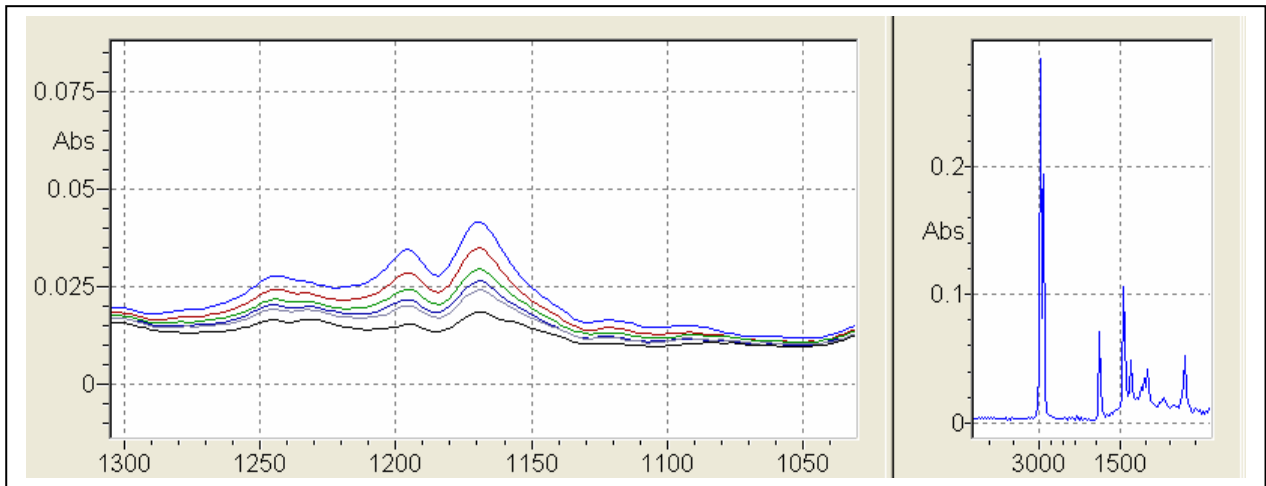


Fig. 2: Typical PLS model using 6 blends from B10 to approx. B33 for the analysis of FAME in Biodiesel blends

Report of PLS Calibration	
FAME [%]	6 samples representing different blends from biodiesel
33.330	
25.000	
20.000	
16.670	
14.280	
10.000	

Calibration Table:	
Algorithm:	PLS I
Number of components:	1
Number of references:	6
Range[1]:	400.00 - 4000.00
Centered data:	Yes
Component:	FAME
Number of factors:	1
Correlation coeff: 0.99832	
MSEP:	0.00280
SEP:	0.05288
X Leverage warnings:	1
Y Residual warnings:	0

Conclusion

The best quality of infrared spectra is to reach with transmission mode spectra. But this treatment is time consuming, a calibration must be done for the one cell and the treatment includes some possible problems regards the thickness. The liquid cell must be checked. Necessary time frame is about 10 minutes per sample. The ATR-technique can be handled within 2 minutes and is not so expensive because there is no need of cyclohexane to prepare standard solution and sample solutions for the analysis.

This simple test over 6 samples correlates already with 0.99832 as found for the correlation coefficient. This is a rough model showing that it will work properly. Natural the result gets much more robust with more standards inside. Material in use was biodiesel and mineral oil from the market and not standardised solutions.

Instrumentation:

IRPrestige-21
IRsolution Software
DuraSamplIR with KRS-5 crystal

Measurement technique:

Single ATR, 2 µm penetration

Time Balance sample preparation:

Classical = 5 to 10 min

Modern ATR = 30 sec

The given specifications serve purely as technical information for the user. No guarantee is given on technical specification of the described product and/or procedures.