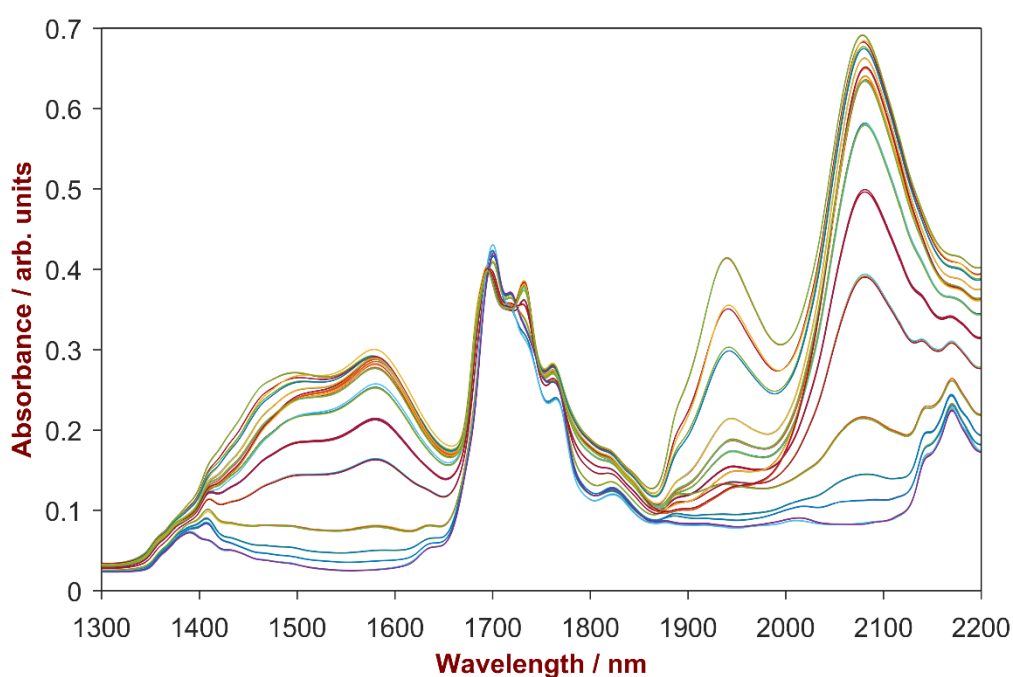


# Moisture analysis of ethanol-hydrocarbon blends by Vis-NIR spectroscopy



This Application Note shows that visible near-infrared spectroscopy (Vis-NIRS) can determine water content in ethanol-hydrocarbon blends. Vis-NIRS is a fast alternative to conventional lab methods: it accelerates raw material inspection, process monitoring, and final product control.

# Method description

## Introduction

Water damages both fuel tanks and engine parts. Rust and corrosion in the tank create hard particulates that are passed along by the fuel, causing engine wear. Component life is also shortened by water etching, erosion, cavitation, and spalling. It can also cause indirect damage through microbial growth and fuel oxidation. Water has always caused rust and corrosion, but modern fuel systems are much less tolerant than older, lower pressure systems. Manufacturers now specify zero free water must reach the engine. [1]

To ensure zero free water fallout, water must be kept below its saturation point so that it stays dissolved. Saturation points vary from roughly 0.005% to 0.18% based on temperature and on the petro diesel / biodiesel ratio.

Removing excess water from fuel can be a challenge. The most effective approach is to take every reasonable measure to prevent water from entering tank, and to monitor it regularly. [2]

ASTM Standard D6304 (Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration) calls for the use of coulometric KF titration in the manufacturing, purchase, sale, or transfer of petroleum products to predict the moisture content of petroleum products. [3] However, KF titration involves toxic solvents and requires a well-trained operator for highly reproducible results, resulting in relatively high costs for routine analysis. In this application note, it is demonstrate that Vis-NIRS is a good alternative to routine KF titration for saving both time and money.

## Experimental

51 ethanol-hydrocarbon blend samples with moisture values from coulometric KF-titration were provided to evaluate the correlation between changes in spectral data and moisture values. The constituent value ranges from 0.0026–1.2016% moisture. 47 samples were used to develop a prediction model; four samples were used for external validation.

The spectra were collected in transmission mode on a NIRS XDS RapidLiquid Analyzer over the full wavelength range (400–2500 nm). The samples were placed in quartz glass cuvettes with 2 mm path length and analyzed at room temperature. The software package Vision Air 2.0 Complete was used for data acquisition, data management and development of the quantification method, see Table 1 / Figure 1.

Table 1: Used equipment and software.

Equipment	Metrohm code
NIRS XDS RapidLiquid Analyzer	2.921.1410
NIRS quartz glass cuvettes, 2 mm path length	6.7401.210
Vision Air 2.0 Complete	6.6072.208



Figure 1: The NIRS XDS RapidLiquid Analyzer was used for spectral data acquisition over the wavelength range from 400 nm to 2500 nm.

## Results

Figure 2 shows the dominant water bands with a correlation between increasing moisture content and increasing absorbance. These water absorption bands at 1380–1670 nm and 1875–1990 nm were used to build a quantitative prediction model.

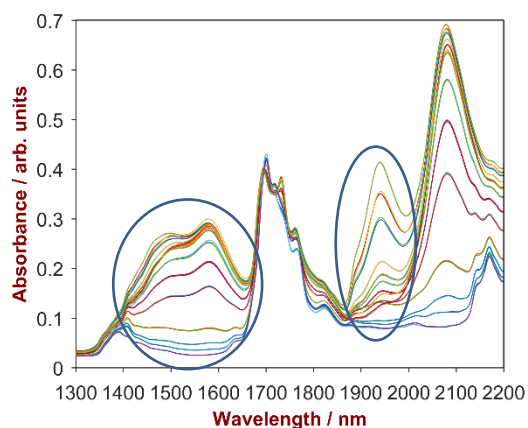
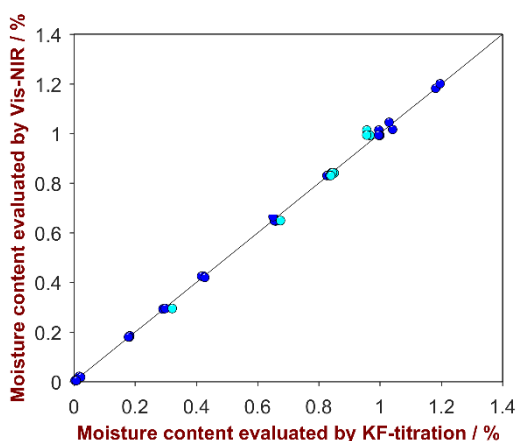


Figure 2: Non pre-treated spectra of 47 ethanol / hydrocarbon blends samples in the region of 1300–2200 nm. The typical water bands around 1400 nm and 1900 nm are highlighted.

## Method description

A Partial Least Squares (PLS) model using 6 factors shows a high correlation between the provided reference values and the calculated values ( $R = 0.999$ ) and low Standard Errors (SEC = 0.0097%, SECV = 0.0116% and SEP = 0.0120%), see **Figure 3**. Parameters used for method development and the figures of merit are listed in **Table 2**.



**Figure 3:** Correlation plot of the predicted moisture content Vis-NIRS versus the KF titration values. Displayed are the calibration (blue) and the validation data (turquoise).

**Table 2:** Results of the quantitative method development for moisture content.

Regression model	PLS with 6 factors
Pre-treatment	none
Wavelength range	1380–1670 nm, 1875–1990 nm
$R^2$	0.999
SEC	0.0097%
SECV	0.0116%
SEP	0.0120%
Range	0–1.2% moisture

Internal cross-validation was applied to verify the performance of the quantitative models during development. The model was then externally validated using new samples, each one measured in triplicate, the results of which are summarized in **Table 3**.

**Table 3:** Comparison of moisture content of external validation samples determined by KF titration with Vis-NIR prediction.

	NIR [%]	KF TIT [%]
Sample 1	$0.426 \pm 0.005$	0.420
Sample 2	$0.665 \pm 0.002$	0.665
Sample 3	$0.827 \pm 0.007$	0.831
Sample 4	$0.056 \pm 0.010$	0.058

### Summary

This application work demonstrates how Vis-NIRS provides a rapid and accurate method for the determination of moisture content in ethanol-hydrocarbon blends. The spectral changes observed in an NIR spectrum correlate to the amount of moisture in a given sample. The results of the calibration and validated for moisture determination by Vis-NIR spectroscopy showed that it can predict moisture within  $\pm 0.0120\%$ .

### References

- [1] <http://www.mycleandiesel.com/pages/ProblemWater.aspx>
- [2] <http://www.mycleandiesel.com/pages/SolutionWater.aspx>
- [3] <https://www.astm.org/Standards/D6304.htm>