

Measurement of Water in Ethanol - Using an Aspectrics MC2750 EP-NIR for Concentrations of Ethanol Greater Than 90% v/v.

Summary: A calibration was developed for predicting moisture in corn-based ethanol using an Aspectrics Encoded Photometric Near-Infrared (EP-NIR) MC2750 spectrometer and a 2mm pathlength transmission dip probe. Moisture content ranged from 0.2 – 10%. This preliminary study proves the MC2750 EP-NIR to be an effective tool to predict the moisture content of ethanol, particularly when ethanol concentrations are 90% v/v or

Introduction

An Aspectrics MC2750 EP-NIR spectrometer was coupled to an external halogen Near-IR source and a Specac process transmission multimode fiber probe in order to test the device's capability to quantify the percentage volume of water in ethanol.

In order to quantitate unknown samples, a multivariate PCR model was developed from the Near IR spectra of all samples. The resulting PCR quant model is characterized by an R^2 greater than 0.9970 for both the calibration and validation data sets as well as an RMSEC of 0.07% and RMSEP of 0.14 % (values consistent with the precision of the sample blending volumetric method).

The implementation of standard quantitative approaches utilizing the extended spectral range allowed for a robust PCR model (values were consistent with the precision of the sample blending volumetric method)

Experimental

Samples:

- Denatured corn-based ethanol samples diluted with distilled water to concentrations ranging from 0.2 to 10.0% were used for this experiment.
- 15 calibration standards and 16 independent validation standards were prepared by volumetric pipetting (see table 1). Please note that the independent validation standards included water concentrations not covered in the learning set in order to test not only the accuracy, but also the instrumental response linearity in validation.
- The precision of the reference method is approximated at 0.06 ml for a 10 ml pipette (i.e. relative error of 1.2%) resulting in a precision of the reference method of 2.4%. relative.

Table 1: Quantitative results of water prediction in ethanol

R ² RMSEC N	Water in Ethanol Calibration Stats			Water in Ethanol Validation Stats		
		0.9997			0.9970	
		0.07			0.20	
		15			14	
Sample #	Ref (%)	Calc (%)	Diff (%)	Ref (%)	Calc (%)	Diff (%)
1	0.2	0.19	-0.01	2.0	1.95	-0.05
2	0.2	0.20	0.00	2.0	1.97	-0.03
3	0.2	0.22	0.02	2.0	1.98	-0.02
4	0.2	0.18	-0.02	5.0	5.00	0.00
5	0.2	0.19	-0.01	5.0	4.94	-0.06
6	5.0	5.18	0.18	5.0	5.03	0.03
7	5.0	5.02	0.02	5.0	5.02	0.02
8	5.0	4.94	-0.06	5.3	5.33	0.07
9	5.0	4.98	-0.02	5.3	5.36	0.10
10	5.0	4.90	-0.10	5.3	5.33	0.07
11	10.0	9.93	-0.07	5.3	5.39	0.13
12	10.0	9.94	-0.06	8.0	7.84	-0.16
13	10.0	10.01	0.01	8.0	7.66	-0.34
14	10.0	10.09	0.09	8.0	7.69	-0.31
15	10.0	10.00	0.00			

Apparatus:

- Aspectrics MC2750 EP-NIR spectrometer covering the 1375-2750 nm range.
- External halogen Near IR source.
- Specac process transmission multimode fiber probe (600 microns polyimide) with 2 mm pathlength.

Data Collection:

- All spectra were collected using Aspectrics, Inc.'s RTSS Chemometrics software package. Data collection parameter was 60-second time integration. Calibration and validation samples were analyzed in 5 and 4 replicates, respectively, collecting a new background between each assay.
- Data treatment consisted of:
 - Calculating absorbance spectra (from single beam intensity spectra) using open beam configuration as a background.

- Developing Principal Component Regression (PCR) based methods for the measurement of moisture content.

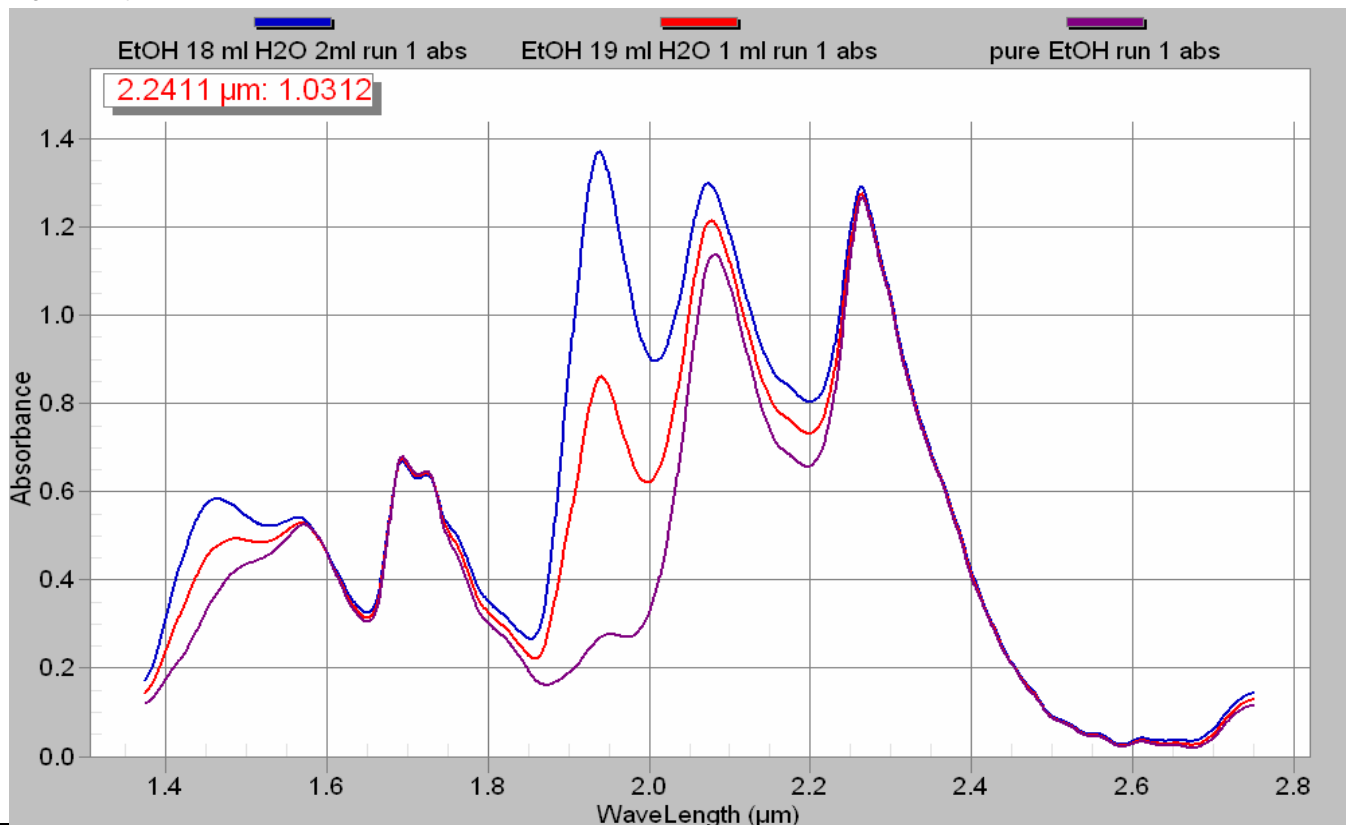
Results & Discussion

Spectral ranges 1.375 – 1.548 micron and 1.743 – 2.273 (figure 1) were selected for the development of the chemometrics methods. Two outliers were removed from the validation set as their spectra were clearly different from the spectra of the other repeat analysis of the same samples.

As illustrated by the individual assays quantitative results reported in table 1 and illustrated by figures 2 and 3, we observe that:

- Strong correlations between concentrations are visually noticed in the spectral range of 1.4 – 1.55 micron and 1.85 – 2.00 micron, characteristic of water, and in the C-OH region between 2.00 and 2.2 micron.

Figure 1: Typical water in ethanol spectra collected with an Aspectrics MC2750 EP-NIR



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- The precision of the calibration is ascertained through the RMSEP of the validation set, which was 0.14% v/v. Considering the maximum concentration for water (10% v/v), this value is consistent with the precision of the reference method (1.2% relative).
- A majority of this deviation originates from the 8.0% sample, which suggests a pipetting error during sample preparation.

Conclusion

The results from this experiment confirm that ability of the Aspectrics MC2750, with an extended range transmission DIP probe, to accurately measure low level water in ethanol samples.

Furthermore, this experiment highlights that the accuracy of study is highly dependent on the precision of the reference method (volumetric).

Measurement of Water In Ethanol Using an Aspectrics MC2750 - Calibration Results

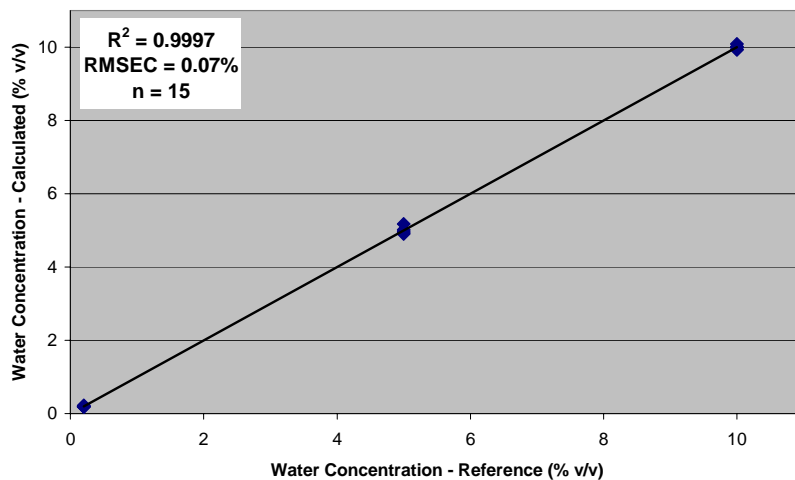


Figure 2: Calibration Results for the measurement of water in ethanol using an Aspectrics MC2750 EP-NIR with an extended range 2mm pathlength transmission dip probe.

Measurement of Water In Ethanol Using an Aspectrics MC2750 - Validation Results

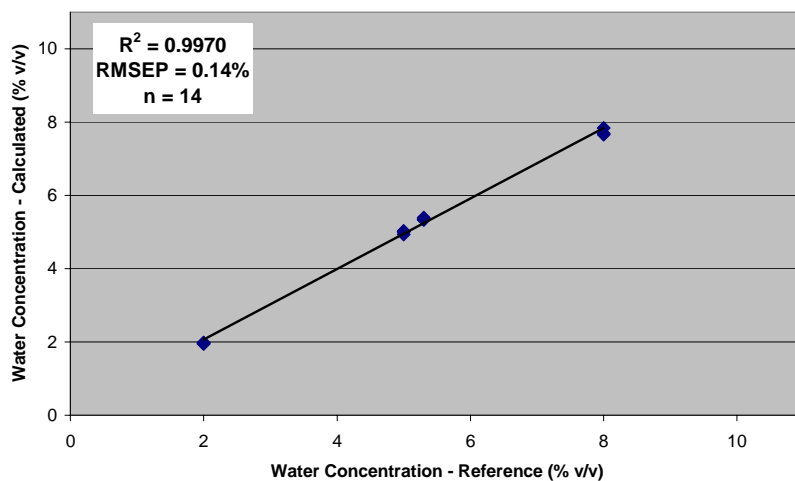


Figure 3: Validation results for the measurement of water in ethanol using an Aspectrics MC2750 EP-NIR with an extended range 2mm pathlength transmission dip probe.



Figure 4:
Aspectrics
MC2750 EP-NIR
spectrometer
with an
extended range
transmission
dip probe (600
microns
polyimide) 2 mm
pathlength.