Determination of Ethyl and Methyl Alcohols in a Mixture Using NIR Spectroscopy with a Fiber Probe

Simultaneous determination of ethyl and methyl alcohols in a two-component aqueous solution using near-infrared (NIR) spectroscopy and a fiber-optic transflection probe have been investigated. The calibration model was trained using a designed set of 25 samples mixed in accordance with the diagonal experimental design. High prediction accuracy of both ethanol and methanol obtained (root mean-square error RMSE < 0.2% and determination coefficient R^2 = 0.999 by cross-validation) indicates that NIR-spectroscopy suits well for their precise simultaneous analysis in aqueous mixtures in-line using fiber-optic probes. The optimal wavelength intervals and spectral preprocessing methods for the qualitative and quantitative analysis of lower alcohols have been shown.

Nowadays chemical, pharmaceutical, and food industries experience a large need for analytical methods enabling rapid and accurate determination of methanol and other lower alcohols in real time. The analysis should be performed in complex mixtures, sometimes in the medium of a running technological process using built-in fiber probes. In-line monitoring of industrial processes is required to prevent the process course going beyond the normal course and to provide necessary product quality. Currently, the main instrumental method for analyzing the chemical composition of rectifiers and distillates is gas-liquid chromatography. This is a reliable and highly accurate method, but it is expensive and requires a rather long analysis time.

Optical spectroscopy in the NIR-range equipped with multivariate data analysis with chemometrics represents a viable alternative to the separation methods. NIR-spectroscopy with fiber-optic probes integrated into the process medium enables sampling-free analysis of lower alcohols in real time, for example, during the course of an industrial distillation process.

To develop an optical spectroscopic technique for the quantitative analysis of ethanol and methanol in rectifiers and distillates, it is necessary to build a mathematical model on a representative set of training samples.

In the present work, a set of calibration samples has been created using a diagonal experimental design for two-component mixtures [A. Bogomolov, *Diagonal designs for a multi-component calibration experiment*, Anal. Chim. Acta **951** (2017) 46-57]. It is based on filling the diagonals of a Latin square, which intrinsically excludes correlation of the component concentrations in an aqueous mixture of methanol and ethanol. Besides, this scheme provides sufficiently full and uniform coverage of the experimental space (Fig. 1).

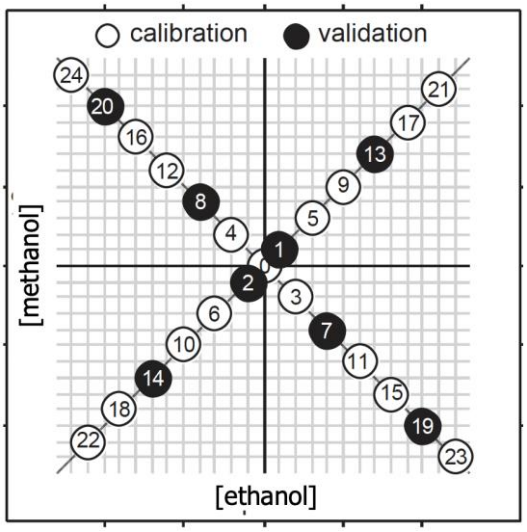

Figure 1. Diagonal design for a two-component mixture of ethanol and methanol.

Chemically pure methyl alcohol (99.9%) and ethyl alcohol (99.9%), as well as the distilled water were used for sample preparation. The exact component concentrations in water varied between 0% and 19.2% for both components.

NIR spectra of the samples in the range 900–1750 nm were obtained using Matrix-F spectrometer (Bruker, Germany) through a transflection (fiber probe with an adjustable pathlength by art photonics (Berlin, Germany). In the present work the probe slit was set to 2.95 mm, which corresponds to the total optical pathlength of 5.9 mm, considering that the NIR-light passes the way twice due to the mirror reflection (Fig. 2). Air (no sample) spectrum was used as a reference.

Figure 2. Transflection probe tip for the NIR-spectroscopic analysis of ethanol-methanol mixtures.

NIR-spectra of the mixture samples are presented in Fig. 3. The most informative spectral range of 1100–2000 nm was chosen for the data analysis. In the calibration dataset, each sample was presented by three replicate spectra to account for the measurement reproducibility, when the probe was removed from the sample and reinserted.

As the raw spectra are dominated by the strong signal of water at 1450 nm (Fig. 3, top), their second derivatives were used instead to emphasize the spectral differences of the vibration overtones of -OH, $-CH_3$ and $=CH_2$ groups of the alcohols (Fig. 3, bottom).

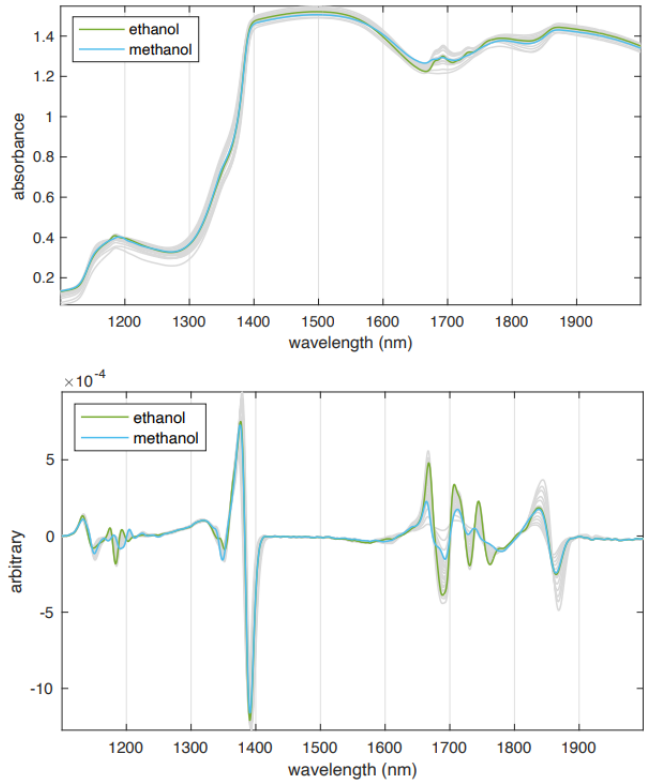

Figure 3. NIR-spectra of 25 designed samples of aqueous ethanol-methanol mixtures: raw data (top) and second derivative by Savitzky-Golay (bottom). Spectra of pure ethanol and pure methanol solutions in water (samples 23 and 24 in Fig. 1, respectively) are highlighted.

The derivative spectral data in the selected region were used to build a partial least-squares (PLS) regression models for ethanol and methanol. Plots of predicted versus reference concentrations of the alcohols and the respective model validation statistics are shown in Fig. 4. The PLS-prediction models for ethanol and methanol were built with 4 and 5 latent variables (LVs), respectively. The prediction accuracies were estimated using the root mean-squares error (RMSE) and coefficient of determination (R^2) statistics segmented cross-validation (with segments formed by three replicate spectra of the same sample). Model validation using the built-in test set (black circles in Fig. 1) at the same model complexities (nLV) gives similar results: RMSE of 0.21% and 0.11% for ethanol and methanol, respectively. The obtained 1% relative (to the concentration range) prediction errors for both alcohols prove the capability of NIR-spectroscopy to perform their simultaneous determination in their water mixtures with high accuracies. The models can be further improved by means of optimization of data processing techniques, such as variable selection and thorough adjustment of parameters of the derivation algorithm.

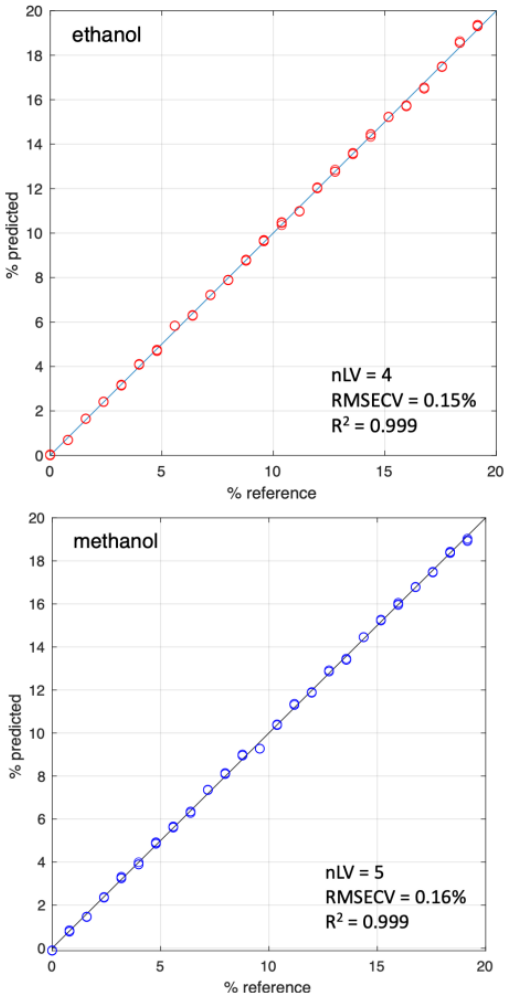

Figure 4. PLS-predicted versus measured plots for concentrations of ethanol (top) and methanol (bottom) in the mixture samples. The prediction accuracy is represented by the root mean-squares errors and R^2 coefficients of cross-validation.

The experiments performed have shown that ethanol and methanol in their water mixtures can be accurately determined in-line. Their estimated prediction accuracies are sufficient for the majority of practical industrial applications. The NIR-probe application enables sampling-free in-line analysis of various objects and processes in real time.