# Determination of Ethyl and Methyl Alcohols in a Mixture Using ATR-FTIR Spectroscopy with a Fiber Probe

**We demonstrate the feasibility of simultaneously quantifying ethanol and methanol in a two-component aqueous solution using infrared (IR) spectroscopy with a fiber-optic attenuated total reflection (ATR) probe. A calibration model was trained using a designed set of 25 samples mixed in accordance with the diagonal experimental design. Data analysis revealed the optimal wavelength intervals for accurate determination of both alcohols. Calibration models were built for ethanol and methanol. The root mean-square error of cross-validation was below 0.10% for ethanol and 0.14% for methanol (determination coefficient $R^2 > 0.999$ in both cases).**

**Such a high accuracy of ethanol and methanol quantification in aqueous solutions using a fiber optic ATR probe suits well for a wide range of practical applications, including real-time process monitoring and quality control.**

Nowadays chemical, pharmaceutical and food industries experience a large need for analytical methods enabling 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 essential for maintaining stable operation within normal parameters and ensuring consistent 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.

A viable alternative to the chromatographic analysis of alcohols is the optical spectral analysis. High-resolution infrared spectra allow tracking even small differences in the similar spectra of homologues. The modern ATR-probes using the polycrystalline infrared (PIR) fiber technology have a good transmittance in the highly informative fingerprint region of spectra. Fiber-based optical probes allow analysis without labor-intensive sample preparation and even, in some cases, without sampling. ATR-probes can be integrated into the production pipelines for real-time analysis, for example, into an industrial distillation process. To develop an optical technique for analyzing rectifiers and distillates, it is necessary to build a mathematical model based on spectral data and train it on a representative set of training and test samples. Such a set was created using the diagonal design scheme for a two-component experiment [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 a two-component aqueous solution, where the components are represented by methanol and ethanol (Fig. 1). Chemically pure methyl alcohol (99.9%) and

ethyl alcohol (99.9%), as well as the distilled water were used for sample preparation. Concentration ranges of both alcohols varied between 0% and 19.16%.

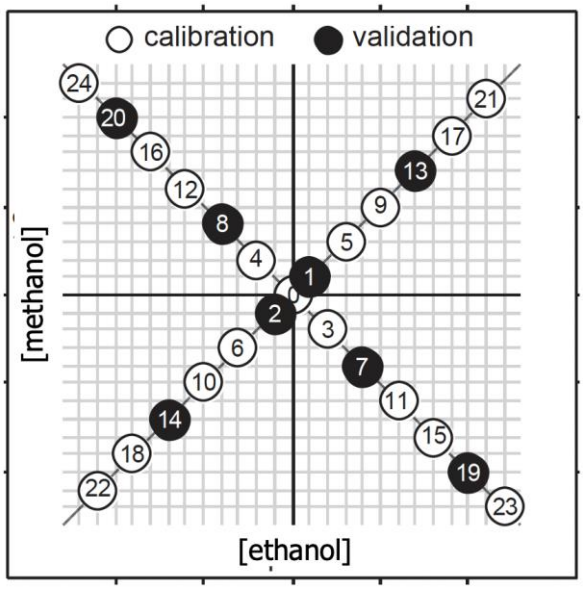


*Figure 1. Diagonal design for a mixture of two components.*

IR spectra of the samples were obtained through a PIR fiber **ATR-probe (art photonics, Germany)** with a diamond ATR crystal. The probe was connected to Matrix-F FTIR-spectrometer (Bruker, Germany). Absorbance spectra were acquired with the resolution of 8 $cm^{-1}$ at 64 accumulations. Air spectrum was taken as a reference.

Fig. 2 shows the fingerprint region of the IR-spectral data of the studied ethanol-methanol mixture samples. Intense peaks at 1015 $cm^{-1}$ and 1055 $cm^{-1}$ are assigned to stretching vibrations of the C–O bond of methanol and ethanol, respectively. The observed difference in fundamental frequencies caused by the bond's chemical environment enables simultaneous determination of both alcohols in aqueous solutions using ATR IR-spectroscopy and chemometrics.

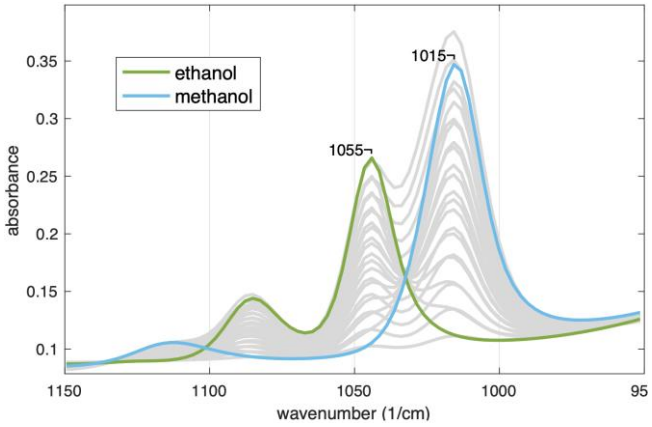


*Figure 2. Fingerprint region of IR-spectra of 25 designed samples (Fig. 1) of aqueous ethanol-methanol mixtures. Spectra of the pure alcohols are highlighted.*

For quantitative analysis, 75 spectra were taken (three replicates for each of 25 designed samples). Calibration models for the determination of ethanol and methanol were built in the selected spectral region (Fig. 2) using partial least-squares (PLS) regression algorithm. The data was mean centered prior to the modelling; no spectral preprocessing was used. The model quality was characterized by root mean-square errors of sample-based segmented cross-validation (*RMSECV*) and by independent prediction (*RMSEP*) on the integrated validation set. The validation samples built into the experimental design (Fig. 1) were used for the prediction only, while the model was trained on the calibration subset only in that case. Three latent variables were used for PLS-model building, as corresponds to the minimum of *RMSEP*. Determination coefficient $R^2$ of both models was above 0.999, which is an indicator of a very high accuracy of prediction. The respective validation statistics is presented in Table 1.

*Table 1. Root mean-square errors of cross-validation and prediction for ethanol and methanol calibration models obtained by PLS-regression algorithm with tree latent variables.*

| Component | *RMSECV*, % | *RMSEP*, % |
|---|---|---|
| Ethanol | 0.12 | 0.10 |
| Methanol | 0.18 | 0.14 |

The accuracy of component prediction is also illustrated by predicted versus measured plots shown in Fig. 3.

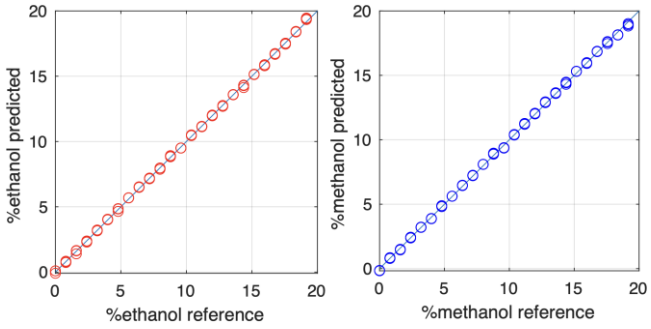


*Figure 3. Predicted versus measured plots for ethanol (top) and methanol (bottom) PLS-regression models with 3 LVs (modelling statistics is given in Table 3).*

Very high prediction accuracy of ethanol and methanol (*RMSEP* is 0.10% and 0.14%, respectively; and $R^2$ > 0.999) from the same FTIR-spectrum obtained using a PIR fiber-based ATR probe, illustrates a very broad applicability of the suggested method. The models can be similarly built or adopted for the analysis of lower alcohols in their industrial mixtures, e.g. for in-line monitoring of chemical, biotechnological, and other processes.