Comparison of different mid-infrared ATR probes for simultaneous analysis of ethanol–methanol mixtures

Qualitative and quantitative analysis of liquid samples can be efficiently performed by attenuated total reflection (ATR) spectroscopy in the mid-infrared (MIR) region. Implemented in a fiber-optic probe, the method allows for the accurate in-line determination of components in complex technogenic or natural mixtures. In particular, the ATR-probe can be immersed into the environment of a running technological process to enable sampling-free determination of a component concentration in real time. The choice of an ATR probe for a specific analytical task depends largely on the choice of the appropriate fiber type. Two widely used fiber materials that are transparent in the MIR range of electromagnetic radiation are polycrystalline infrared and chalcogenide infrared glasses (PIR and CIR, respectively) manufactured by art photonics GmbH (Berlin, Germany). Different probes have maximum transmittance in different spectral regions. Therefore, the probe type selection should be based on the chemistry of components being analyzed. In this comparative study, the efficiency of CIR and PIR ATR fiber probes was examined in simultaneous determination of ethanol (C_2H_5OH) and methanol (CH_3OH) in their binary aqueous mixtures over a wide range of component concentrations using Fourier-transform (FTIR) spectroscopy. Calibration models obtained using a designed set of 25 mixture samples have shown that both probe technologies are well suited for the accurate determination of these lower alcohols. Recommendations are given to the selection of a probe choice depending on the nature and complexity of the analyzed media, available budgets and other practicability factors.

Methyl and ethyl alcohols belong to the most important fuels and chemical raw materials. The world production of each of them is estimated at more than one hundred billion liters per year and shows a steady growth. In addition, a significant amount of ethanol is produced and consumed as part of alcoholic beverages (about 26 billion liters per year according to WHO). These lower alcohols are often present as a mixture. In some cases, they are mixed intentionally (biofuels, solvents). In others, the presence of one as an impurity in the other is undesirable (pure reagents, food ethanol). Thus, simultaneous determination of ethyl and methyl alcohols is an important analytical problem. The content of both alcohols must be determined not only in the finished product, but also during the process of its chemical or biotechnological production.

Figure 1. Attenuated Total Reflection (ATR) probe. The working spectral range is determined by installed fibers, e.g., CIR or PIR.

Chemically informative optical spectroscopy in the MIR range is ideally suited for the analysis of homologous (i.e. structurally similar) molecules of ethyl and methyl alcohols. For an in-line analysis, the spectrometer is equipped with fiber-optic ATR probes. Using the probe allows measurements to be taken at a distance of tens of meters from the device.

Modern ATR probes using the polycrystalline infrared PIR fiber technology have a good transmittance in the range of **600-3100 cm^{-1}** that includes the highly informative so-called region of “fingerprints”. At the same time, the chalcogenide-based CIR cables and probes have better transmittance in the range **1550-9000 cm^{-1}**, which contains mainly the stretching vibration bands of water and hydrocarbon residues. Together, these materials cover almost the entire MIR range. **PIR ATR probe (diamond ATR crystal, with PIR fibers, 1.5 m total length)** and **CIR ATR probe (Cubic Zirconia ATR crystal, with CIR fibers, 1.5 m total length) manufactured** by art photonics GmbH were used in this study.

Calibration models for ethanol and methanol were developed using a set of 25 samples mixed in accordance with the diagonal design scheme containing a built-in validation subset [A. Bogomolov, *Diagonal designs for a multi-component calibration experiment*, Anal. Chim. Acta **951** (2017) 46-57]. Chemically pure methanol (99.9%) and ethanol (99.9%), were diluted in the distilled water. The resulting pure component concentrations varied from 0% to 19.16%.

Absorbance MIR spectra were acquired with a resolution of 8 cm^{-1} and 64 accumulations on a Matrix-MF FTIR-spectrometer (Bruker, Germany). The air spectrum was used as a reference. Three replicate spectra were obtained for each sample were taken, for a total of 75 spectra.

Fig. 2 shows the spectral data used for calibration. The characteristic C–O stretching bands of methanol and ethanol are observed in the fingerprint region using the PIR probe (Fig. 2, top). The stretching vibrations of the C–H bond are observed against the background of a strong water signal in the 3200–2600 cm^{-1} region of MIR-spectra obtained using the CIR probe (Fig. 2, middle). In the latter case, the application of the Savitzky-Golay second-derivative transform increases the spectral contrast (Fig. 2, bottom).

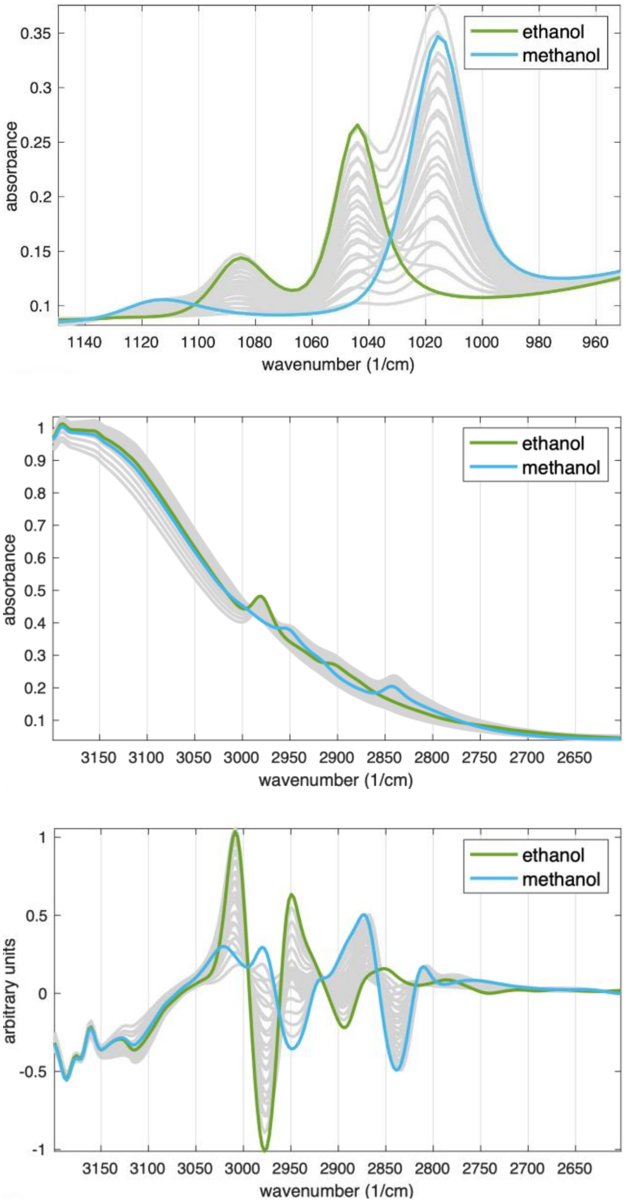

Figure 2. FTIR-spectra of 25 aqueous ethanol-methanol solutions obtained with PIR (top) and CIR (middle) probes. The second derivative spectra of the CIR probe data are shown in the bottom panel. Spectra of pure ethanol and methanol solutions at maximum concentrations are highlighted.

Calibration models for the determination of ethanol and methanol were built using the partial least-squares (PLS) regression algorithm. No spectral preprocessing was applied to the PIR probe data. The second-derivative transformation (as in Fig. 2, bottom) was applied to the spectra obtained with the CIR probe, as it leads to simpler PLS models (fewer latent variables, nLV) and higher prediction accuracy. The quality of the models was characterized by the root mean-square errors (RMSE) and the coefficients of determination (R^2) of segmented cross-validation with the segments formed by the data of individual samples (Fig. 3).

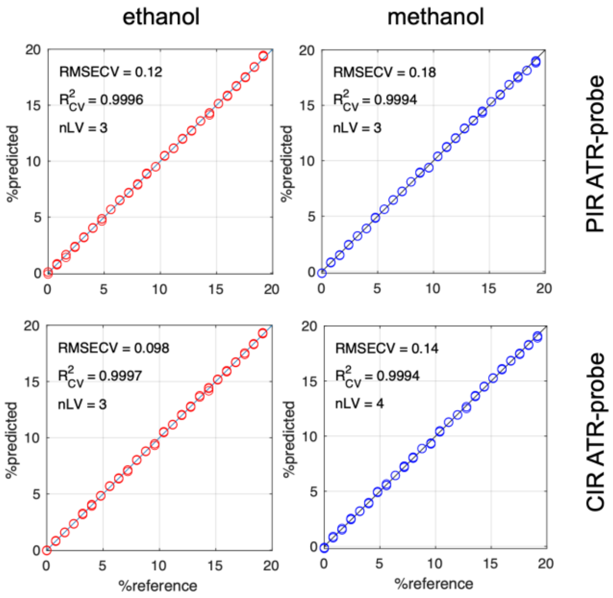

Figure 3. Cross-validation statistics of PLS calibration for methanol and ethanol based on the data obtained by PIR and CIR probes.

The values of the determination coefficients $R^2 > 0.999$ indicate very high prediction accuracy in all models presented in Fig. 3. These results indicate that both the PIR and CIR fiber based probes examined in this study are perfectly suited for the ATR spectroscopic analysis of ethanol-methanol mixtures. Calibration models can be built using a single calibration set and predicted from a single spectrum of the component mixture. Ethanol and methanol concentrations can be predicted with absolute root mean-square errors of about 0.1%, i.e. the relative error (compared to the concentration range) is less than 1%. Although the developed methods are spectrally based on different MIR regions and the corresponding characteristic vibrations of alcohols, they are suitable for a wide range of practical applications. Spectrum preprocessing and chemometric analysis successfully compensate for the weaker absorption bands and interferences of aliphatic C–H vibrations (CIR probe), compared to the C–O bands of alcohols in the fingerprint region (PIR probe). At the same time a more advanced PIR-probe with a diamond ATR-crystal may be preferable for analyzing complex samples, such as industrial process medium and multicomponent mixtures containing hydrocarbons.