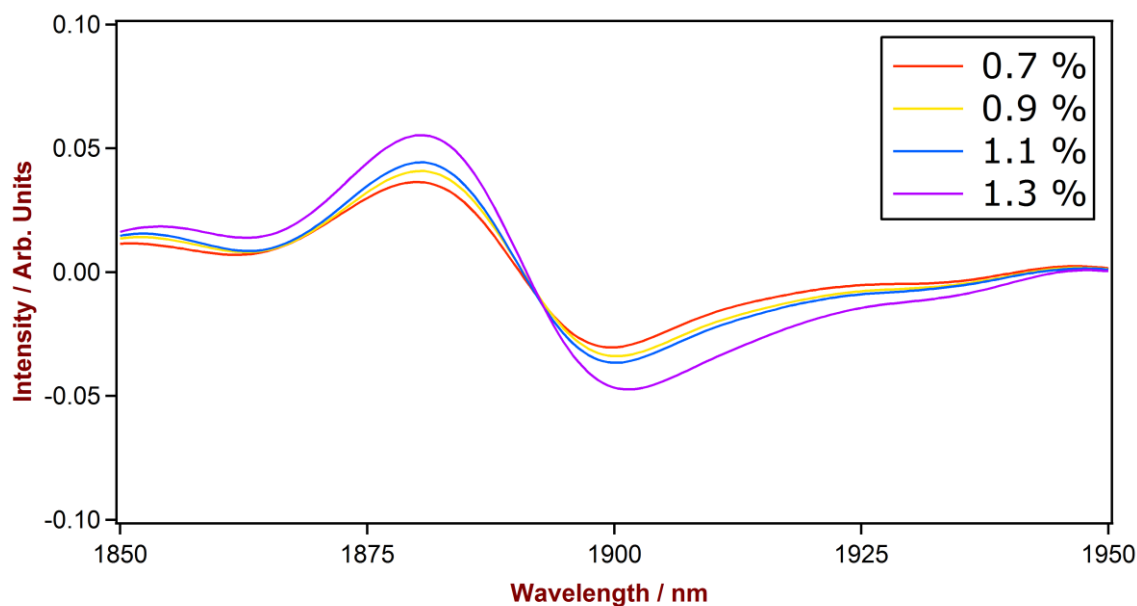


NIR Application Note NIR-36

Moisture content and pH value in crude tall oil (CTO)



This Application Note shows that near-infrared spectroscopy (NIRS) can simultaneously determine water content and pH value in crude tall oil samples (CTO). This technology is a faster alternative to conventional lab methods and therefore accelerates raw material inspection, process monitoring, and final product control.

Method description

Introduction

The pulp and paper industry, especially the production of office paper, tissues, and paper-based packaging material, is one of the largest industrial sectors worldwide. Around 400 million tons are produced per year. Therefore, the kraft process is the most applied method. It is a chemical (mixing with a hot mixture of water, sodium hydroxide, and sodium sulfide) and mechanical (milling) treatment of wood chips. If coniferous pain wood is converted into wood pulp (main component of paper), crude tall oil (CTO) arises as a useful by-product. It consists primarily of fatty acids and resin acids of varying levels, depending on factors such as the species of pine tree, geographic location, or climate. After fractional distillation, tall oil (or liquid rosin) finds use as biofuel, additive in inks, as cement binder, or emulsifier for asphalt. Usability and quality is depending mainly on moisture content and pH value. These important parameters can be determined simultaneously using visible-near-infrared spectroscopy (Vis-NIRS) as a fast alternative to conventional lab methods.

Experimental

20 tall oil samples of known moisture content (0.7–2.5%) and pH value (3.8–5.4) were provided. 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 disposable glass vial with 4 mm path length and analyzed at room temperature, see **Tab. / Fig. 1**.

Tab.1: Used equipment.

Equipment	Metrohm code
NIRS XDS Rapid Liquid Analyzer	2.921.1410
NIRS 4 mm disposable glass vials	6.7402.010
Vision 4.03 Software	6.6069.102



Fig. 1: A NIRS XDS RapidLiquid Analyzer equipped with 4 mm NIRS disposable glass vials were used to generate the spectral data in true transmission mode over the full wavelength range (400–2500 nm).

For the prediction model of moisture content, 14 spectra were used to calibrate, and 6 used to validate the model. The pH model was built with 15 spectra for calibration and 5 for validation. The reference values necessary for the development of a quantitative model were provided by the customer using their lab reference analytics.

Vision, with its Partial Least Squares (PLS) algorithm, was used to develop quantitative prediction models for moisture content and pH value in crude tall oil. Therefore, absorption bands of the NIR-range (1120–2240 nm) were chosen. The spectral data were pre-treated using a 2nd derivative to get rid of multiplicative baseline effects. Internal cross validation (leave-one-out method) was applied to verify the performance of the derived quantitative model.

The optimized regression models were then used to predict moisture content and pH value on 4 unknown samples.

Results

Moisture content:

The spectral range in the region 1850–1950 nm is the region of water bands. The spectrum shows a great correlation between the moisture content and the absolute absorbance value, see **Fig. 2**.

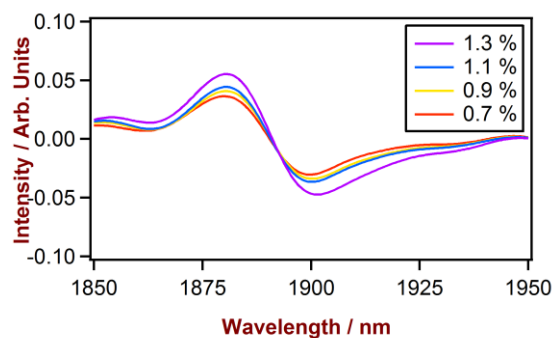


Fig. 2: Spectra of crude tall oil samples around 1850–1950 nm. It is the region, where water bands occur in this region. The moisture content varies between 0.7% and 1.3%. A good correlation is observable.

The manual spectral observations (**Fig. 2**) are confirmed by the good Figures of Merit (FoM in **Tab.2**).

Method description

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

Regression model	PLS with 2 factors
Pre-treatment	2 nd derivative, 10 nm segment size
Wavelength range	1120–2240 nm
R ²	0.833
SEC	0.065%
SEV	0.097%
SEP	0.032%

Conclusion

The feasibility study demonstrates that Vis-NIR spectroscopy is a rapid technology to determine moisture content and pH value in crude tall oil.

pH value:

The spectral range in the region 1475 –1550 nm shows a great correlation between the pH value and the absolute absorbance value, see **Fig. 3**.

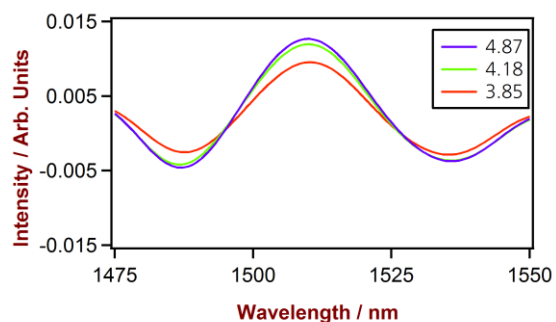


Fig. 3: Spectra of crude tall oil samples around 1475–1550 nm. The pH value varies between 3.85 and 4.87. A good correlation is observable.

The manual spectral observations (**Fig. 3**) are confirmed by the good Figures of Merit (FoM in **Tab.3**).

Tab. 3: Results of the quantitative method development for pH value

Regression model	PLS with 2 factors
Pre-treatment	2 nd derivative, 10 nm segment size
Wavelength range	1120–2240 nm
R ²	0.839
SEC	0.209
SEV	0.340
SEP	0.102