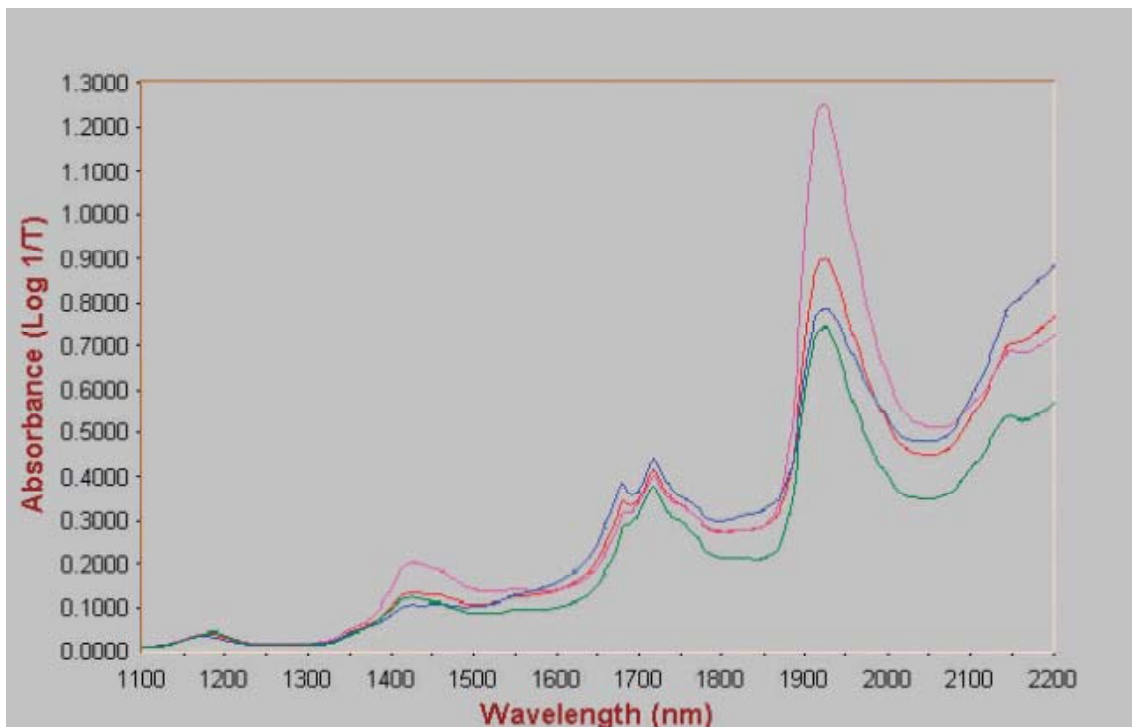


Process monitoring in a butyl acetate production stream using near-infrared spectroscopy



This Application Note demonstrates feasibility for implementing a NIR measurement in the esterification process of butyl acetate. The developed NIR method showed excellent analytical performance equivalent to that obtainable with a more time-consuming GC method.

Method description

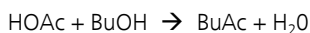
Introduction

In 1999, 350 million pounds of butyl acetate were demanded in the consumer market. Butyl acetate is used increasingly throughout industry as a lacquer solvent (for wood furniture and automotive topcoats), for adhesives, pharmaceutical solvents, and as an extraction solvent for fermentation processes. In this paper, the utility of near-infrared (NIR) spectroscopy will be explored for measurement of the compounds involved in the production of butyl acetate.

NIR spectroscopy is a safe, rapid, and nondestructive method that may be implemented directly in a process stream through fiber optics. The real-time information provided by the NIR allows control and optimization of the production process. This results in thousands or even millions of dollars of savings in analytical costs, improved production, and increased quality of the product.

Experimental

Sample spectra were obtained on a FOSS NIRSystems 5000 laboratory monochromator equipped with a Liquid Analyzer module. Since this instrument is no longer available, the equivalent and recommended instrument configuration is the NIRS XDS RapidLiquid Analyzer. A quartz cuvette with a 1 mm pathlength was selected to scan the samples over the 1100 to 2500 nm wavelength region. Butyl acetate is produced in the reaction of an acid with an alcohol shown in the equation below.



Calibration samples were created by obtaining three different production samples and spiking the samples at various levels with acetic acid (HOAc), water (H₂O), butyl acetate (BuAc), and butanol (BuOH) in an experimentally designed manner to eliminate intercorrelations between the various components. HOAc was present at levels of 23 to 66%, H₂O was present at levels of 5 to 18%, BuAc was present from 27 to 67%, and BuOH was present from approximately 1 to 9%. These concentration ranges represent the expected levels during the production process. The control parameters for this process are HOAc, H₂O, and BuAc.

Results and discussion

The absorbance spectra of the pure components are displayed below in Fig. 1. As the purpose of this study is to demonstrate feasibility for implementing a measurement in process, the spectra are limited to 1100–2200 nm region. This is because process NIR instrumentation uses fiber optics which attenuates the spectrum above 2200 nm, which makes the 2200–2500 nm region of little use for spectroscopic measurement.

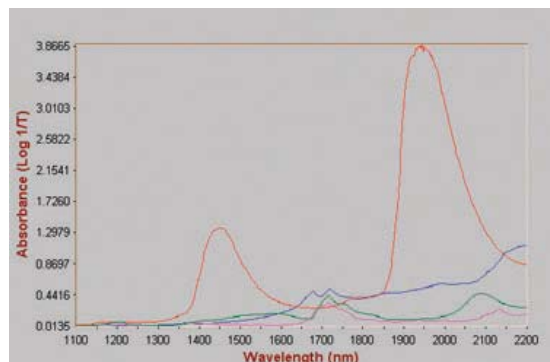


Fig. 1: Pure component raw spectra

The absorbance bands in the NIR region are very broad and highly overlapped, and the baseline exhibits some variation, which makes it difficult to find unique features for each material in the raw absorbance spectra. However, with the application of a second-derivative, the spectra are enhanced and unique features are much easier to see, as evident in Fig. 2.

Absorbance bands for each constituent in the samples may be identified which uniquely identify that particular constituent, as shown in Figures 2a–2c.

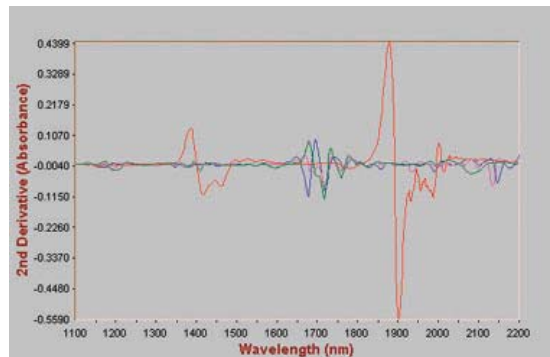


Fig. 2a: Second-derivative spectra of pure components – note raw spectral peak maxima are converted to peak minima using the second-derivative transform. Water has a strong absorbance band near 1450 nm, acetic acid (HOAc) has unique bands at both 1690 and 2150 nm, and butyl acetate (BuAc) demonstrates a band near 2130 nm.

Visual: — HOAc — BuOH
Legend: — BuAc — H₂O

Method description

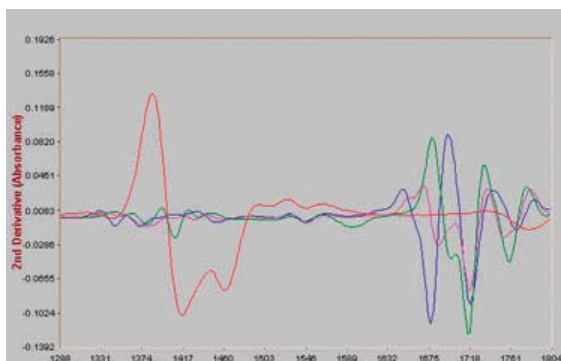


Fig. 2b: Expanded second-derivative of pure components – 1288 to 1804 nm.

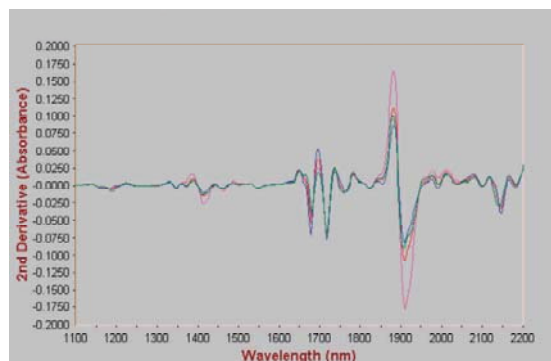


Fig. 4: Second-derivative spectra of calibration samples.

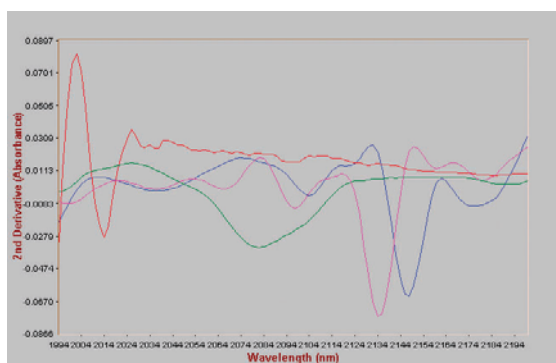


Fig. 2c: Expanded second-derivative of pure components – 1994 to 2194 nm.

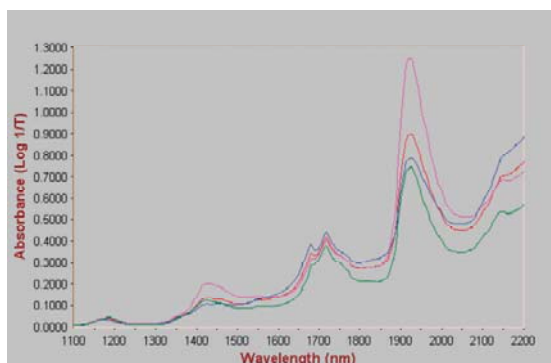


Fig.3: Raw spectra of selected calibration samples.

Figure 3 shows the absorbance spectra of several of the calibration samples. From this figure, it is evident that there is significant baseline variation and overlap of the absorbance bands for the components. If left uncorrected, the effects will significantly limit the ability to quantitatively measure each component in these samples. As shown earlier, the second-derivative math treatment corrects the baseline differences, and enhances the spectral features. The effects of this math treatment on the calibration samples is illustrated in Figure 4 with the baseline variation corrected, and the spectral features enhanced, quantitative calibrations can be developed for the individual components.

Partial least squares (PLS) regression was performed using the second-derivative spectra and associated lab values to build the calibrations for the various constituents. A PLS calibration was developed for HOAc (Figure 5). The correlation (R^2) was quite good at 0.99, with a standard error of calibration (SEC) of 0.81%. The results for H_2O were quite good as well (Figure 6); the R^2 was 0.99, and the SEC was 0.26%. A PLS calibration was constructed for the determination of BuAc (Figure 7). The results were as follows: R^2 was equal to 0.97 and SEC to 1.63%. These results are quite acceptable for controlling this esterification process.

Method description

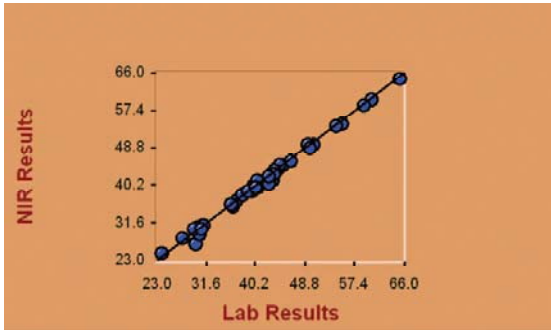


Fig. 5: HOAc calibration results using 4 factors, 1100–2200 nm.

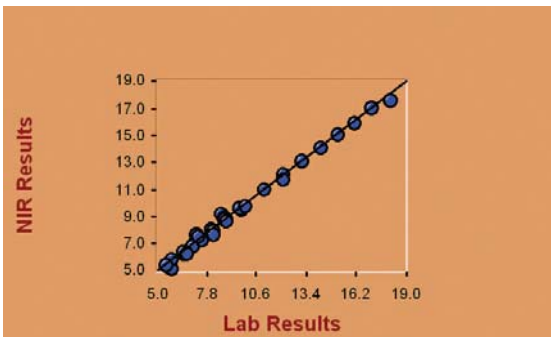


Fig. 6: H₂O calibration results using 2 factors, 1100–2200 nm.

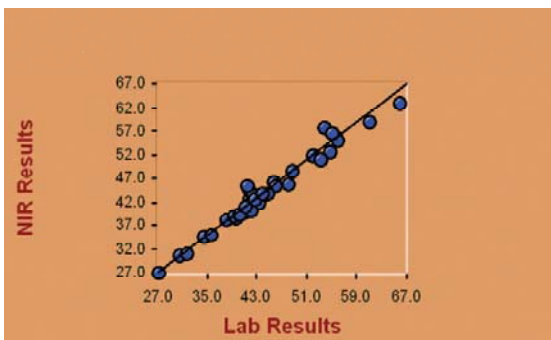


Fig. 7: BuAc calibration results using 3 factors, 1100–2200 nm.

Conclusions

The results presented in this study demonstrate the utility of NIR for the quantification of the control parameters of this ester production stream. The NIR method demonstrated analytical performance equivalent to that obtainable with a more time-consuming GC method. The advantage of the NIR method lies in the ability to perform rapid, continuous in-process analysis updated every few seconds, which allows automated control of the process.