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Monitoring the Hydrolysis of Acetic Anhydride Using In-Situ Raman Spectroscopy and Novel Multivariate Data Analysis – Band-Target Entropy Minimization (BTEM)

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Abstract

With the increasing demand for novel process analytical technologies in recent years, Raman spectroscopy has been one of the powerful choices for in-situ reaction monitoring. In this paper, we discuss the use of in-situ Raman spectroscopy and novel multivariate data analysis method namely band-target entropy minimization (BTEM) to monitor the hydrolysis of acetic anhydride to acetic acid. In-situ Raman spectroscopy is employed to continuously measure the spectrum of reaction mixture for a few hours time. The collected reaction spectra are then subjected to BTEM in order to elucidate the pure component spectra and the concentration profiles of the observed components. In addition, a comparison study between univariate and multivariate data analysis on the reaction spectra is also presented.

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1.0 Introduction

Reaction monitoring has been one of the major interests for chemical engineers in order to optimize chemical processes as well as to use the monitoring information for process control. Recently, one of the process analytical techniques that has seen much improvement and advances is Raman spectroscopy. From discovery of Raman scattering in 1928, this technique has really progressed tremendously, overcoming many impediments faced in the past. Earlier models of Raman spectrometers faced problems including weak intensity, inefficient light collection and detection, and fluorescence interferences. These have been superseded by newer models having more sophisticated features such as charged coupled devices (CCD) array detectors, low cost lasers, holographic optical elements, and fiber optics probe. Another factor that undoubtedly helped created a Raman renaissance was the ready access to multivariate data processing techniques which were developed and tailored to spectroscopy analysis.

In present contribution, we discuss the use of in-situ Raman spectroscopy and novel multivariate data analysis method namely band-target entropy minimization (BTEM) to monitor the hydrolysis of acetic anhydride to acetic acid. Two different in-situ Raman spectroscopy monitoring setups were employed, which were static and flow through modes. The multivariate data analysis includes spectral preprocessing (un-spiking, smoothing, and baseline correction) and band-target entropy minimization (to identify the observed components by recovering their pure component spectra and to generate their concentration profiles).

2.0 Results and Discussion

Two experimental in-situ reaction monitoring modes were planned. In the first mode, the hydrolysis reaction was performed in a quartz cell and was placed directly under a Raman microscope long working distance 50× objective. A 514.5 nm green laser was used as the excitation source and was continuously shined on the quartz cell. Raman spectrum was continuously acquired every 2 minutes during the 1 hour reaction time, and altogether 30 spectra were collected for one reaction. Acquisition time for one spectrum is 60 seconds. Spectral range taken was 100 – 1800 cm^{-1}. A total of 4 reactions with varying concentration of acetic anhydride and water were conducted. Figure 1 shows one of the Raman reaction mixture spectral sets before and after spectral preprocessing.

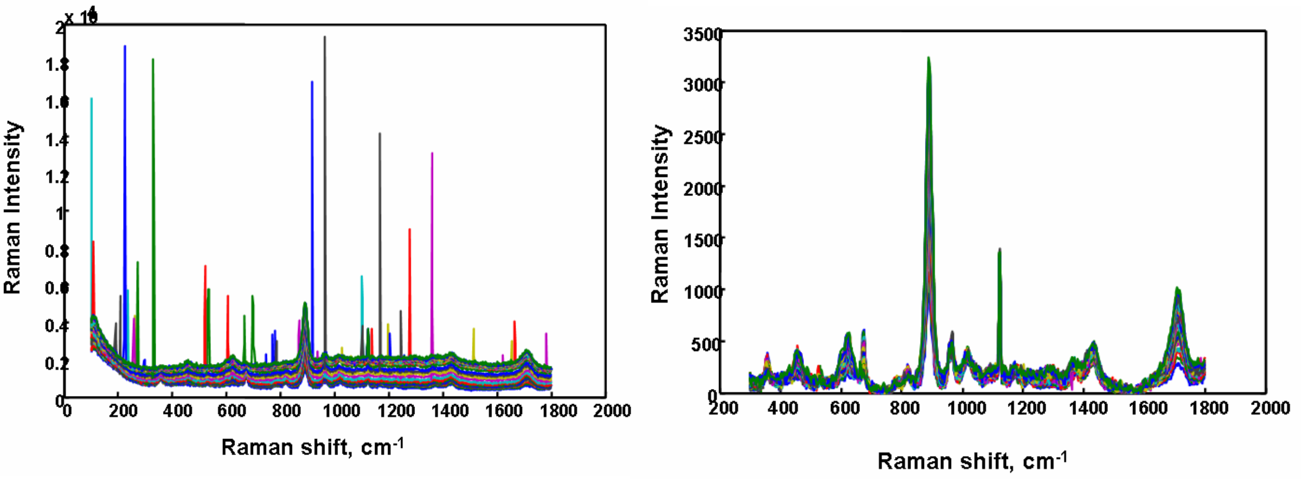

Figure 1. In-situ Raman spectra data before and after spectral preprocessing (reaction 1).

These four-reaction spectral data were collected into one data matrix and were analyzed using BTEM. Three pure component spectra and their concentration profiles were recovered, which belong to acetic anhydride, acetic acid, and white light interference signal.

In the second experimental mode, a flow-through reaction monitoring system was set up. The reactants were placed in a round-bottomed flask and continuously stirred with a magnetic stirrer to ensure well mixing. The flask was immersed in silicon oil bath which kept the temperature constant at 23˚C. A small volume of the flask was pumped continuously by a positive displacement pump into a flow-through cell placed under a Raman microscope 50× objective, and then was recycled back to the flask.

Similar to first set up, a 514.5 nm green laser was used as the excitation source and was continuously shined on the flow-through cell. Raman spectrum was continuously acquired every minute (acquisition time for one spectrum is 60 seconds). Spectral range taken was 100 – 1800 cm^{-1}. From time to time, some perturbations were performed by adding some reactants to the system. The purpose for this perturbation is to break the concentration co-linearity among the observed components, so that BTEM can recover the pure component spectra of the studied system. In this experiment, all together 125 reaction spectra were measured and analyzed. Again BTEM was employed, and three pure component spectra of acetic anhydride, acetic acid, and white light interference and their concentration profiles were recovered.

3.0 Conclusions

The present work studied the use of in-situ Raman spectroscopy coupled with novel multivariate data analysis (BTEM) to monitor the hydrolysis of acetic anhydride. The results show that spectroscopy monitoring coupled with BTEM can be a promising tool in process analytical technology.

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