

# Reaction Monitoring at Elevated Temperature and Pressure Using Fiber Optic Raman Spectroscopy



## Introduction

Raman spectroscopy is possibly the most powerful real-time technique for reaction monitoring. Raman is applicable to aqueous and organic solutions, is simple to use at elevated temperatures and high pressures and fiber optic cable lengths can be over 100 meters in length with little impact on spectral quality.

Since there is a wide range of fiber optic probes available, Raman analysis is applicable to almost any environment.

Prior to the employment of Raman in this case study, reaction monitoring was carried out by removing small quantities of reaction solution, using a specialist valve assembly, and analyzing these samples post-reaction by gas chromatography. This technique is highly unsatisfactory as removing these samples changes the reaction volume, disturbs the reactor pressure, and disturbs the reaction equilibrium.

## A Case Study

Hydrogenation of phenyl acetylene to form styrene and methyl benzene is often used to study the effectiveness of novel catalysts (see Figure 1). The fact that this experiment is carried out at high pressure, high temperature and in the presence of H<sub>2</sub> gas, is no problem for Raman.

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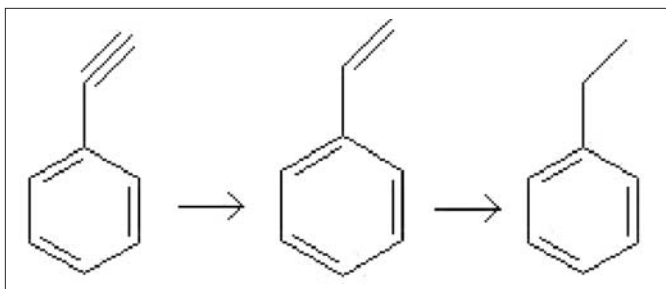


Figure 1. Reaction of interest the hydrogenation of Phenyl Acetylene to form Styrene and finally Ethyl Benzene.

In this case study a stainless steel ‘spinning disk’ reactor was employed (see Figure 2). The reactor consisted of:

- 1) a rotating disk coated in a catalyst
- 2) a reaction solution: heptane (solvent) and phenyl acetylene (starting material) and
- 3) high pressure hydrogen gas

Since this experiment was carried out at high temperature and high pressure, a high temperature/high pressure Raman probe was inserted into the liquid phase of the reactor through a swagelock clamp. The probe had a braised sapphire window to allow use at high pressure.

Raman spectra were automatically acquired every 10 minutes. Over the course of this reaction, 50 spectra were recorded. For reasons of clarity, only three spectra are shown in Figure 3.

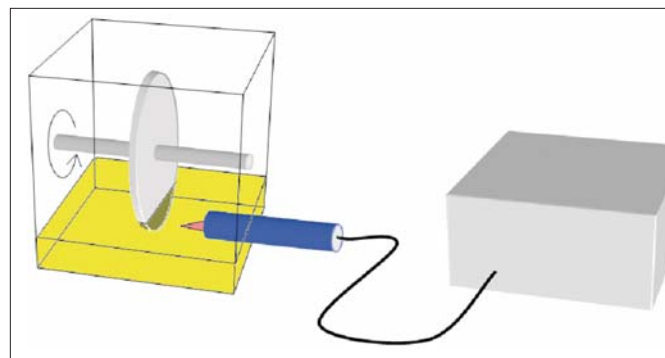


Figure 2. Reactor (left) and Raman spectrometer (right) setup, Raman fiber optic probe shown in blue.

Some spectral differences in the spectra shown are readily apparent. For example, the decrease in the CN triple bond at ca.  $2115\text{ cm}^{-1}$ .

Spectral subtraction of the solvent (Heptane) can be used to make these spectral changes more obvious. This automated technique can be carried out after the reaction has reached completion or in real time as the data are acquired. Figure 4 (Page 3) shows the result of this spectral subtraction. The removal of the contribution of heptane shows that there are significant spectral changes in several regions of the spectrum.

Further analysis using chemometrics was undertaken. Standard solutions of various concentration mixtures were prepared and analyzed using both GC and Raman.

These data were used to develop a chemometric model for quantitative concentration prediction.

Figure 5 (Page 3) shows the implementation of this chemometric-based predictive calibration employed in real time. In this figure, the pathway of the reaction can be seen in % concentration terms. The use of partial least squares (chemometrics) techniques to develop the predictive model means that the complicated and time-consuming business of running GC is no longer required. Thus in all future reaction of this nature, non-invasive, totally automated Raman spectroscopy can be used.

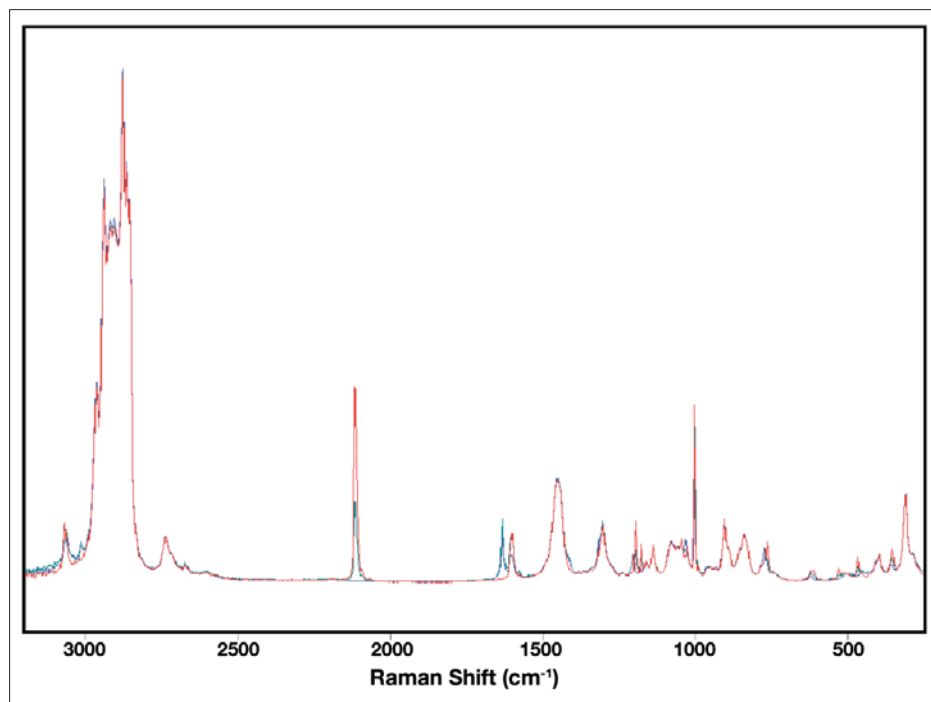


Figure 3. Raman spectra taken at the beginning, middle, and end of the reaction.

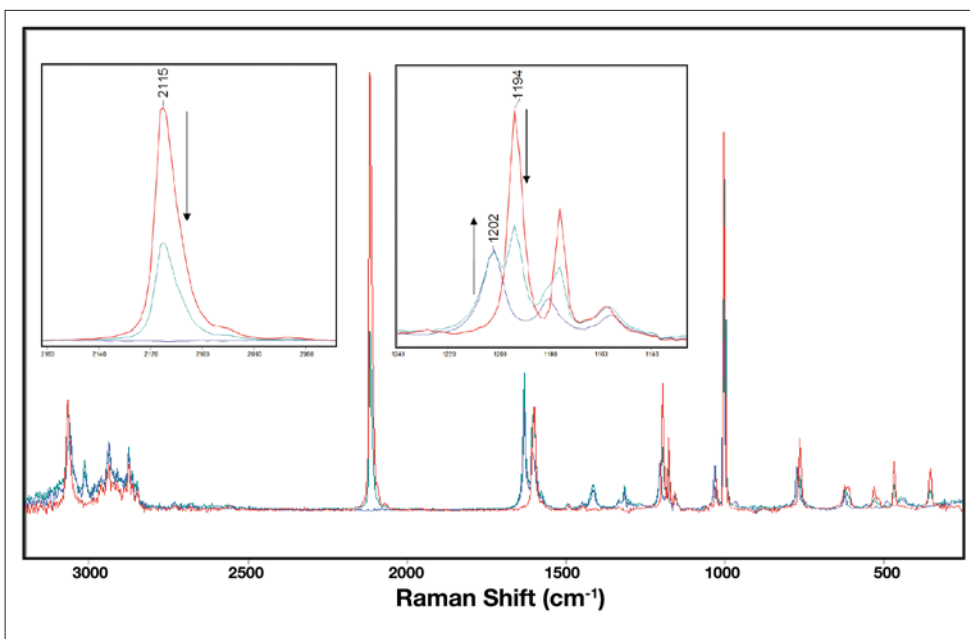


Figure 4. Spectra from Figure 3 with Raman spectrum of solvent (Heptane) automatically spectrally subtracted, spectra differences are more apparent than in the raw data.

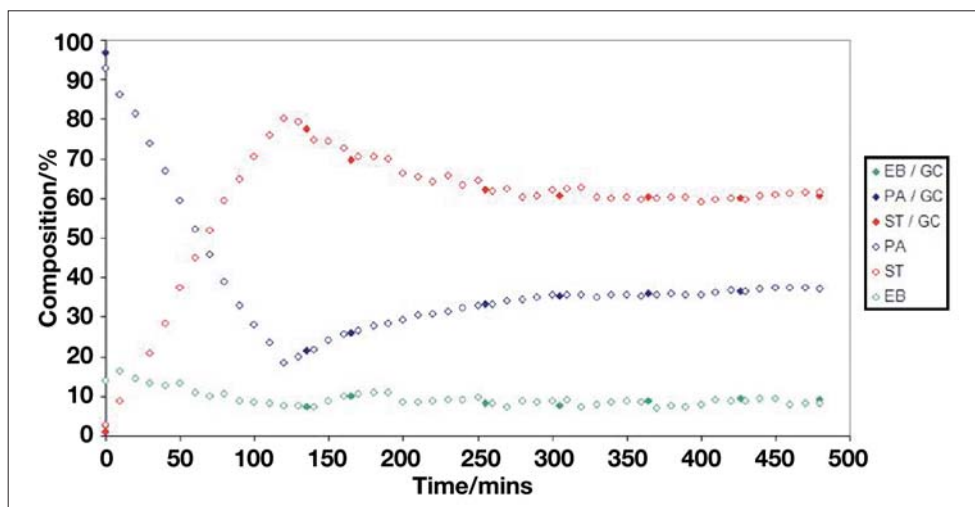


Figure 5. Plot of time V concentration for all three reaction components. Hollow circles represent Raman (chemometric) predictions of concentration, filled circles represent GC results.