Application of Raman Spectroscopy and Chemometric Data Analysis in Reaction Monitoring

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Raman Spectroscopy

- Advantages:
  - Crystalline and amorphous solids / liquids / gases
  - Complementary to FT-IR due to weak CO$_2$ and H$_2$O contributions
  - Glass is a weak Raman scatterer
  - Coupling to fibre optics means remote analysis is possible
Raman Spectroscopy

- Disadvantages:
  - Fluorescence
  - Heating effects
  - Problematic for coloured samples
Multivariate Curve Resolution (MCR)

- **Input:**
  - Data matrix

- **Process:**
  - E.g. Alternating Least Squares (ALS)
    - Non-negativity / equality constraints

- **Output:**
  - Spectral factors
  - Intensity values

\[ D = C \cdot S^T + E \]

- **Data matrix**
- **C**
- **S**
- **E**

- **Intensity**
- **Spectra**
- **Error**
1) Reactor Kinetics Studies

- Reactor kinetic studies via process Raman spectroscopy, multivariate chemometrics, and kinetics modelling
- Acetic anhydride hydrolysis
- 50 mL – 3 L reactors

1) Stirring speed and reaction volume/vessel
2) Variation in reaction temperature

1) Reactor Kinetics Studies
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- Separate analysis of contact (immersion) and non-contact optics

- Reaction vessel type and optical probe analysed separately for chemometric analysis

- Band Targeted Entropy Minimalisation (BTEM)
  - pure component spectra
  - user-specified band-target

1) Reactor Kinetics Studies

Figure 4. Multivariate curve resolution and multilinear regression of NC and C data from 0.5 L Lenz jacketed reactor vessel for 35 °C reaction: NC data (a) BTEM spectral estimates with abstract $V^T$ vectors and (b) corresponding MLR relative concentration profiles, and C data (c) BTEM spectral estimates with immersion probe spectrum and (d) corresponding MLR relative concentration profiles.

1) Reactor Kinetics Studies

Note: NC data – ○; C data – ×; blue line/ curve optimized for C data; red line/ curve optimized for NC data

Figure S3  Raman *in situ* optics problems associated with physical experimental setup conditions
1) Reactor Kinetics Studies - Summary

- Broad study into difference in stirring rate, reactor size, temperature and ability of different set ups to monitor the kinetics
- No calibration required
- MCR-BTEM successfully used to separate components
- Dissolution and Arrhenius based rate models in agreement with previous literature studies
- Immersion probe gives slight advantage over noncontact probe
- Key limitations:
  - Immersion: bubbles cause anomalous results
  - Non-contact: condensation limits measurements

2) Characterising Hydrogenation Reactions

Figure 1. Raman spectra extracted from the process of cyclohexene reduction to cyclohexane.

Figure 2. Kinetic profile for the disappearance of cyclohexene with Pd/C as the catalyst.

2) Characterising Hydrogenation Reactions

Summary:

- Use peak ratios to monitor known reaction components
- MCR enabled identification of an unanticipated intermediates
- Chemical knowledge still required for interpretation of results and identification of components