developing Raman calibration models for extreme process conditions

Wesley J. Thompson
Brian J. Marquardt
Deep Ocean PAT
Process Conditions

- Harsh environment; near-supercritical seawater
  - Acidic: pH 3-6
  - Temperature: 200-400 °C
  - Pressure: 300 bar (~4409 psi)
- Typical concentrations in vent solutions
  - Sulfate: ~3000 ppm
  - Carbonate: ~1200 ppm
  - Nitrate: ~2 ppm
  - Carbon Dioxide: ~0.13 – 0.5 ppm
  - Hydrogen Sulfide: ~0.13 ppm
- Depth: 3000 m
Raman Ball Probe

- no moving parts
- sapphire spherical lens
- constant focal length and sample volume
- focus is at tangent of sphere
- probe is **ALWAYS** aligned when in contact with sample
- effective sampling of liquids, slurries, powders, pastes and solids
- high sampling precision allows it to be used effectively to monitor dynamic mixing systems (powders/slurries)
- particle size has minimal effect on optical performance (< 1μm – 5mm)
Deep Sea Submersible: Alvin

- Dive length limited by battery power: ~5 hours bottom time
- Limited time at each sample site: ~30 minutes
- Power and communication available through pressure hull
Deep Ocean Raman Data

- Easter Island – diffuse at 22 °C – slow flow
- Gremlin/Hulk – diffuse at 23 °C – fast flow
Sapphire on Water spectrum

- Very discreet peaks
- Multiple point calibration possible
- If peak ratios are consistent then intensity calibration possible as well
Objectives

• Study how high temperature and pressure affect the Raman spectral features of the ballprobe sapphire spherical sampling lens
• Use Design of Experiment generated Raman data to create temperature and pressure models for variable process conditions
• Design experiments to analyze dissolved gas concentrations using temperature and pressure models developed in the previous experiments
Experimental Setup

- Temperature controlled water bath
- Gas mixture controlled by NeSSI and bubbled into water
- HPLC pump
- Swagelok Titanium pressure vessel
- Raman Ballprobe
NeSSI Gas Handling System

- Multiple gases (CO$_2$, H$_2$S, CH$_4$)
- Full DOE with computer controlled dilutions
- Safe handling of noxious/corrosive gases
Sapphire Lines at Pressure and Temperature

Peaks shift slightly, calibration model may be possible
PLS Results: Constant Pressure

Constant Pressure: 100 Bar
Correlation: 0.985
2 PCs

Temperature range from 5-45 °C
PLS Results: Constant Temperature

Constant Temperature: 25 °C
Correlation: 0.99995
2 PCs

Pressure range from 1-300 bar
(15-4409 psi)
The linear response of sapphire to both temperature and pressure seems to allow for a model to be created.
Future Studies

• Extend the range of the temperature model
  ▫ (2-350 °C)
• Study dissolved gas mixtures at varying concentrations using NeSSI for calibration of gasses
  ▫ CO₂, H₂S, CH₄
• Ratio sapphire peaks to other known peaks to study possibility of intensity calibration
• Create full working models of temperature and pressure to auto-calibrate Raman spectra at extreme temperatures and pressures
Acknowledgements

- Charlie Branham
- Dave Veltkamp
- Hamilton Sundstrand
  - Norman Wright
- UW Rome Center