Characterization of a Robust Oxygen Sensor for Process Analysis

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Vapochromic Sensor Compounds

Compounds with poorly packed lattice allow analyte to enter the crystal reversibly.

Compounds possess a UV-VIS-NIR absorbing/emitting solvatochromic chromophore.

Chromophore shifts reversibly when analyte enters the lattice.

**Detectable Analytes**
- Ammonia
- Hydrogen
- Common Solvents
  - Alcohols
  - Esters
  - Amines
- Chlorinated Organics
- Organic Hydrocarbons (BTEX)
- Oxygen
- Carbon Dioxide (in development)
- Hydrogen Sulfide (in development)

Large void spaces in the crystal lattice allow analyte gases and vapors to move easily in/out of the crystal.

Emission Quenching Oxygen Sensing

Long lived excited states can be quenched by oxygen molecules via energy transfer – “phosphorescence”

Ruthenium tris bipyridyl and platinum porphyrin are commonly used oxygen sensing compounds

Current Sensor Limitations:
• Singlet oxygen produced in the quenching event is very reactive and the emitter gradually decomposes
• Due to the decomposition, the photostability of the sensors is poor

Advantages of Vapochromic Sensors:
• Photostable and therefore no need for lifetime or phase measurement
• Porous structure enhances response of the sensor
• Simple intensity measurements can be performed

Sensor Structure has a Large Void Space

- Bulky ligands and cations create large void space in crystal lattice
- Oxygen selective substituent increase the oxygen affinity of the sensor

Enhances the response time and reversibility of sensor
Advantages of Fiber Optic Sensors

- Fast response
- Inexpensive
- Robust
- Stable
- Low Power
- Sensitive
- Small
Oxygen Sensor Applications

Applications

1. Biological Processes (Fermentors, Proteomics)
2. Industrial Processes (Reaction Vessels, Corrosion)
3. Ocean Processes (Argo floats, SeaGliders, Moorings)
4. Environmental Monitoring (Air Quality: submarines, space shuttle, airplanes, industrial work areas, ...)

Analytical Performance of the Sensor
Digital NeSSI Gas Generation System
“New Sampling Sensor Initiative”

Features of NeSSI Gas Generation System:
1. Four stage dilution, able to produce and maintain known oxygen concentrations (6 ppm to 100% oxygen in the gas phase and 0.3 ppb to 42 ppm oxygen in the liquid phase)
2. Records spectrum, temperature, pressure and oxygen reference simultaneously
3. Fully automated system, set and forget capability
Photostability of the Oxygen Sensor

The sensor was placed in a sealed insulated box at 21% oxygen for 12 weeks under illumination from a 405 nm light source.

This is equivalent to more than 6 years of measurements taken every 30 seconds using a 100 ms gated LED.

PtTFPP = Pt((pentafluorophenyl)porphyrin), PTFEM = polytrifluoroethylmethacrylate

<table>
<thead>
<tr>
<th>Compound/ Polymer</th>
<th>Stability (%/day)</th>
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</thead>
<tbody>
<tr>
<td>VCS/Teflon</td>
<td>0.12</td>
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<tr>
<td>PtTFPP/PS</td>
<td>9.2</td>
</tr>
<tr>
<td>PtTFPP/PTFEM</td>
<td>0.5</td>
</tr>
</tbody>
</table>

PLS Model in Mixed Gases

5 replicates at each concentration
Concentration range: 0 - 21% Oxygen

- $R^2 = 1$
- 3 Latent Variables
- RMSEC = 0.0078337
- RMSEP = 0.010331
- Calibration Bias = -6.4354e-015
- Prediction Bias = 0.0017759

Measured Oxygen Concentration(%)
Predicted Oxygen Concentration(%)

Calibration Data
Predicted Data
Low Range PLS Model in Solution

$R^2 = 0.99964$
3 Latent Variables
RMSEC = 0.27879
RMSEP = 0.29719
Calibration Bias = -3.187e-015
Prediction Bias = -0.068453

5 replicates at each concentration
Concentration range: 1 - 38 μmol/L

$1 \mu\text{mol/L} = 32.5 \text{ ppb}$
**Dissolved Samples Predicted with Gas PLS Model**

- Gas calibration can be performed in minutes while water calibration can take hours for equilibration at each concentration interval.
- Calibrating in gas and applying to liquid greatly increases speed of calibration.
Response Time of the Oxygen Sensor to Air-to-Oxygen/Nitrogen Gas

- VCS/Teflon: 16 ms
- PtTFPP/PS: 39 sec
- PtTFPP/PTFEM: 19 sec

3 replicates averaged

≈100% 98 msec
≈95% 10 msec

≈100% 32 msec
≈95% 7 msec

Response Time of the Oxygen Sensor to Air-to-Oxygen/Nitrogen Saturated Water

Transitioning from Lab to the Process Environment

Fiber Optic Sensor

Cassini probe prototype
Cassini Probe Prototype

Optical Bench:
- A single fiber optic is used to carry the excitation energy to the sensing material and back to photodiode
- The sensing material is mounted on an easily replaceable cartridge at the probe tip
- The cartridge includes an internal reference to correct for temperature and light source variation

Probe Design:
- Robust and process ready
- Equipped with a standard port connector that is compatible with most commercial fermenters
- Probe can be autoclaved while mounted in fermenter without a loss of functionality
- Probe can be mounted in a Parker NeSSI top-mount component for use in a wide range of gaseous and dissolved phase sensing applications
Custom Graphical User Interface

- Probes can be calibrated with a simple two point calibration (air and nitrogen) or single point calibration (air) in the gas phase for dissolved oxygen applications
- Displays calculated oxygen concentration in real-time
- Designed to read multiple probe simultaneously
Sensor Responses

The fiber optic sensor uses a spectrometer and reports data spectrally. Modeled with multivariate methods.

The Cassini probe uses a photodiode and reports data in counts. Modeled with univariate methods.

Because of this we needed to develop new methods to model the Cassini probe.

In the ideal case the quenching of a sensor is modeled with a linear Stern-Volmer equation.

\[
\frac{I_0}{I} = 1 + K_{SV}[O_2]
\]

\(I_0\) = the intensity of a sensor in the absence of oxygen
\(I\) = the intensity of a sensor in the present of oxygen
\(K_{SV}\) = Stern-Volmer Constant
\([O_2]\) = Concentration of oxygen
Stern-Volmer Model in Mixed Gases

1087 training and 33 validation sample
Concentration range: 0 - 30% Oxygen

The resulting RMSEP is comparable to the multivariate PLS models.
Probe-to-Probe Variation: Cartridges

- **Probe #1**
  - Average = 0.02125
  - St. Dev = 0.00007

- **Probe #2**
  - Average = 0.02127
  - St. Dev = 0.0004

- **Probe #3**
  - Average = 0.02133
  - St. Dev = 0.0004
Sterilizing the Cassini Probe

**Stern-Volmer Plot: Pre and Post Autoclave**

- **Post-Autoclave**
  \[ f(x) = 2.42x + 0.96 \]
- **Pre-Autoclave**
  \[ f(x) = 2.35x + 0.98 \]

**Autoclave Procedure**
130 °C at 2 bar for 30 min
Application of the Cassini Probe in a Fermentation
Fermentation Monitoring

- **Simulated Fermentation liquor**
  - 900 mL of synthetic sugar water (5 g/L glucose) was fermented with yeast for 8 hours
  - The solution of sugar was held at 30°C and pH 6 for the duration of experiment.
  - Four 5 mg glucose additions were added when ethanol peak equilibrated. The final total sugar concentration in the reactor was 25 g/L glucose

- **NeSSI Fast-Loop**
  - Cassini Probe and three other PAT
  - 250 mL/min Flow-rate

- Cassini probe was pre-calibrated in the gas phase with a two point calibration (air and nitrogen)
Cassini Probe Response in a Fermenter

![Graph showing Cassini Probe Response in a Fermenter with oxygen concentration and time in hours. The graph indicates yeast addition and glucose additions at specific time points.](image)
Conclusions

Fiber Optic Oxygen Sensor
• Fast response times in both gas and dissolved phase applications
• Excellent sensitivity and dynamic range
• Excellent photostability over time

Cassini Probe Prototype
• Robust and sturdy housing
• Autoclave and steam sterilizable
• One or two point calibration routines
• NeSSI compatible
• Internally referenced
• Custom software interface
Potential for an Ultra-sensitive Oxygen Sensor
Evanescent Oxygen Sensors

Procedure:
A hard-clad fiber was heated with an acetylene torch and drawn to produce a tapered tip at the distal end of the fiber. The tip was then coated with a thin layer of sensing material.

The tapered tip of the fiber optic breaks the total internal reflection in the fiber optic and light is allowed to leak through the cladding to the sensing material.

Advantages over traditional flat faced optical sensors
- Decreased response time
- Increased signal-to-noise
- Reduction of extraneous light
- Improved sensitivity through increased interactions with sensing material
Evanescent vs Flat Faced Sensor

Approximately 100x improvement in evanescent sensor’s signal
PLS Model of the Evanescent Sensor in Mixed Gases

$R^2 = 0.99925$
3 Latent Variables
RMSEC = 0.69405
RMSEP = 0.69699
Calibration Bias = -2.2154e-014
Prediction Bias = 0.045444

20 replicates at each concentration
Concentration range: 0-100% O$_2$

Experimental Design: 0% to 100% to 0% Oxygen in 10% increments, to give a total of 210 samples
The Future Oxygen Sensor

Micro-Oxygen Sensor

- Small footprint
- Low power
- Inexpensive
- Disposable sensing tip
- Wireless and USB communication with computer or mobile phone
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