Setting the Standard for Automation™

Process Applications of a Phase Fluorometric Oxygen Analyzer

Phil Harris

HariTec

Melvin Thweatt

Barben Analyzer Technology, LLC

California or Bust, ISA AD is a Must…….See us in Anaheim 2012

The 57th Annual Symposium of the Analysis Division

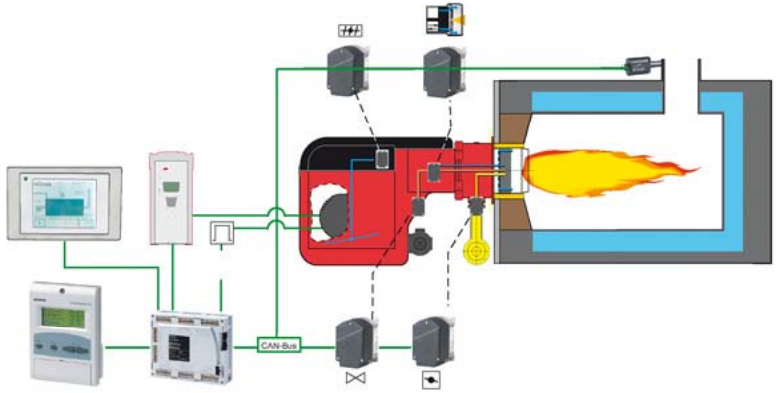
Anaheim, California, USA; 22-26 April 2012

Outline

- Why is Oxygen Measurement so important?
- Technologies Available
- Fluorescence Quenching
  - What is it and how does it operate
- The analyzer
- Applications

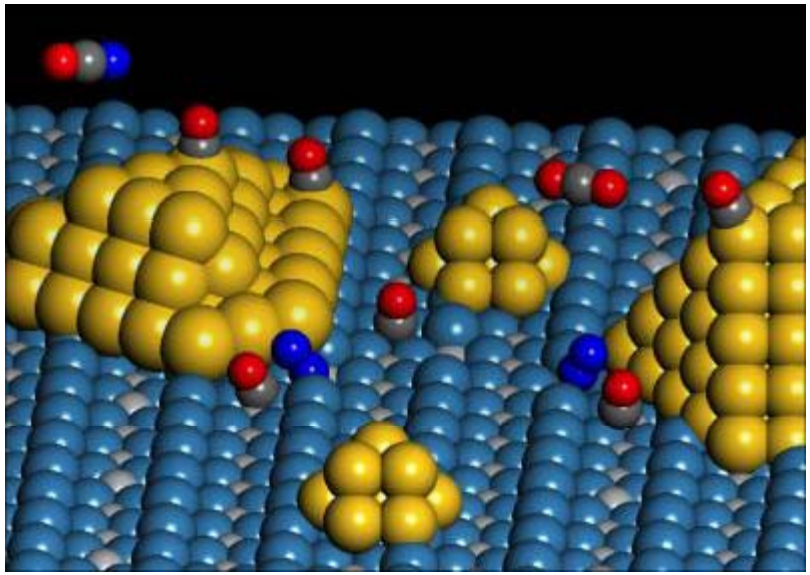
Why Oxygen ?

- Numerous Applications
  - Combustion control
    - Boilers
    - Sulfuric Acid



Why Oxygen ?

- Numerous Applications
  - Combustion control
    - Boilers
    - Sulfuric Acid
  - Catalyst protection
    - Ammonia



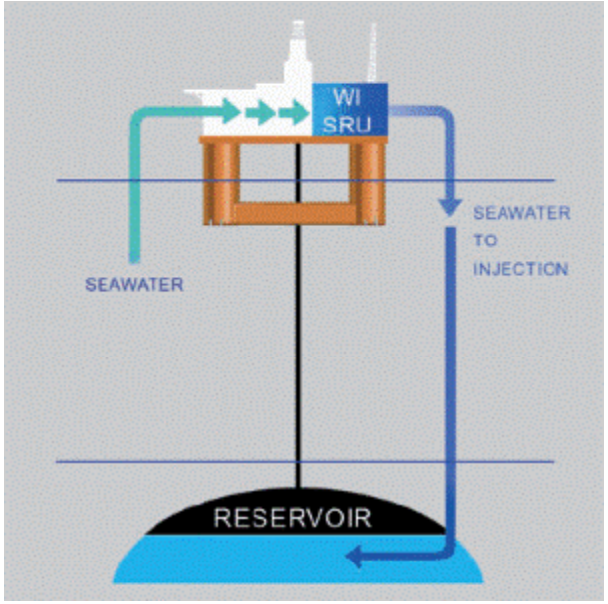
Why Oxygen ?

- Numerous Applications
  - Combustion control
    - Boilers
    - Sulfuric Acid
  - Catalyst protection
    - Ammonia
  - Facility safety
    - Vapor Recovery



Why Oxygen ?

- Numerous Applications
  - Combustion control
    - Boilers
    - Sulfuric Acid
  - Catalyst protection
    - Ammonia
  - Facility safety
    - Vapor Recovery
  - Corrosion Protection
    - Pipelines
    - Boilers
    - “Floodwater” re-injection

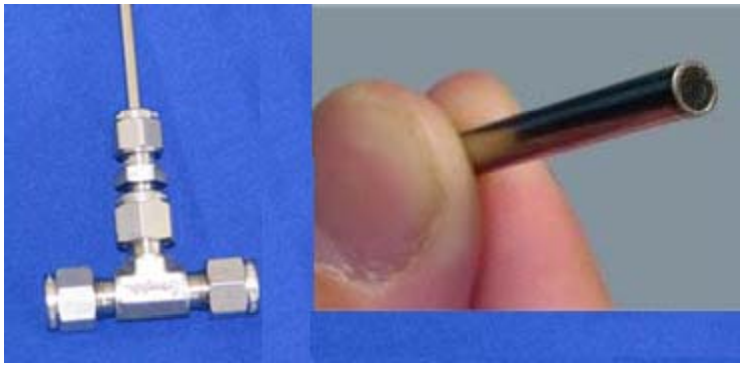


How to Measure Oxygen ?

- Fuel Cell Sensors
  - Sensitive, wide range but can be poisoned
- Clark Cells
  - can be sensitive to fouling, frequent calibration
- Paramagnetic
  - Well established – but relatively high ranges only
- TDL
  - Gaining acceptance – but generally % oxygen
- Zirconia
  - Sensitive from ppb to percent, but issues with combustibles and corrosives

Fluorescence Probes

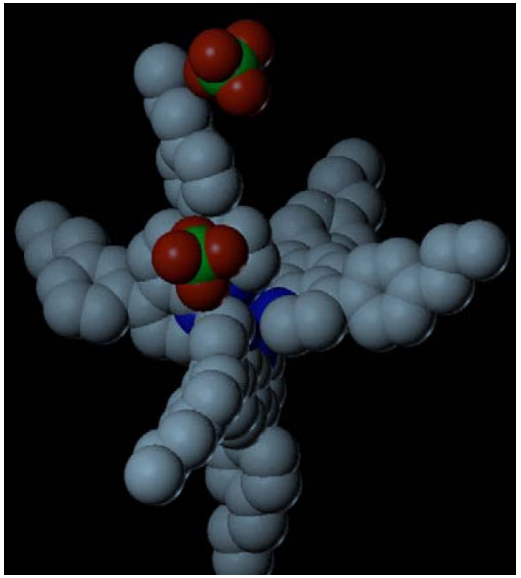
- Simple fiber-optic probe that can be put right into the process – be incorporated in an existing analyzer or sample system – or have a custom system built around it
- Same technology for liquid and gas phase applications
- Wide ranges (from parts per billion aqueous and ppm gas phase to percent levels of oxygen)
- Interference free, accurate, doesn't fall asleep, robust, poison resistant (even to high H_2S), no electrical components in contact with sample

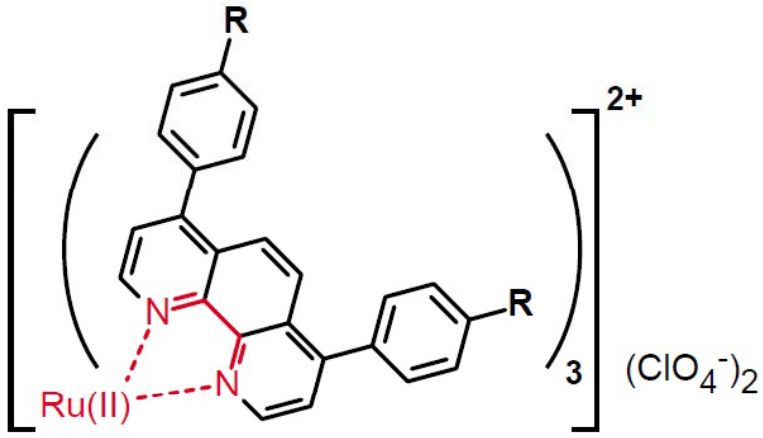




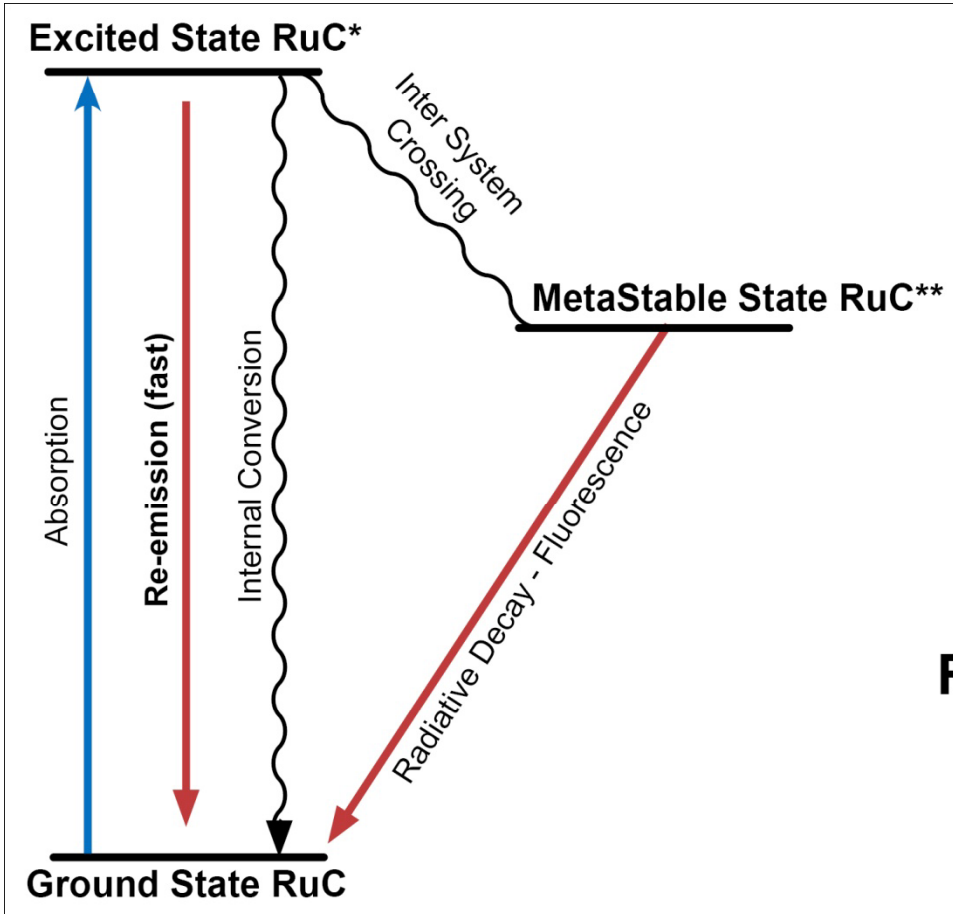
Ruthenium Complexes

- Large metal / organic molecules – Ruthenium diimines
- tris(4,7 bis(4-propylphenyl)-1,10 phenanthroline)–ruthenium(II) perchlorate
- Let's just call him RuC (ruthenium complex)





Fluorescence by Ruthenium Complexes



$$RuC + h\nu \xrightarrow{\text{absorb}} RuC^*$$

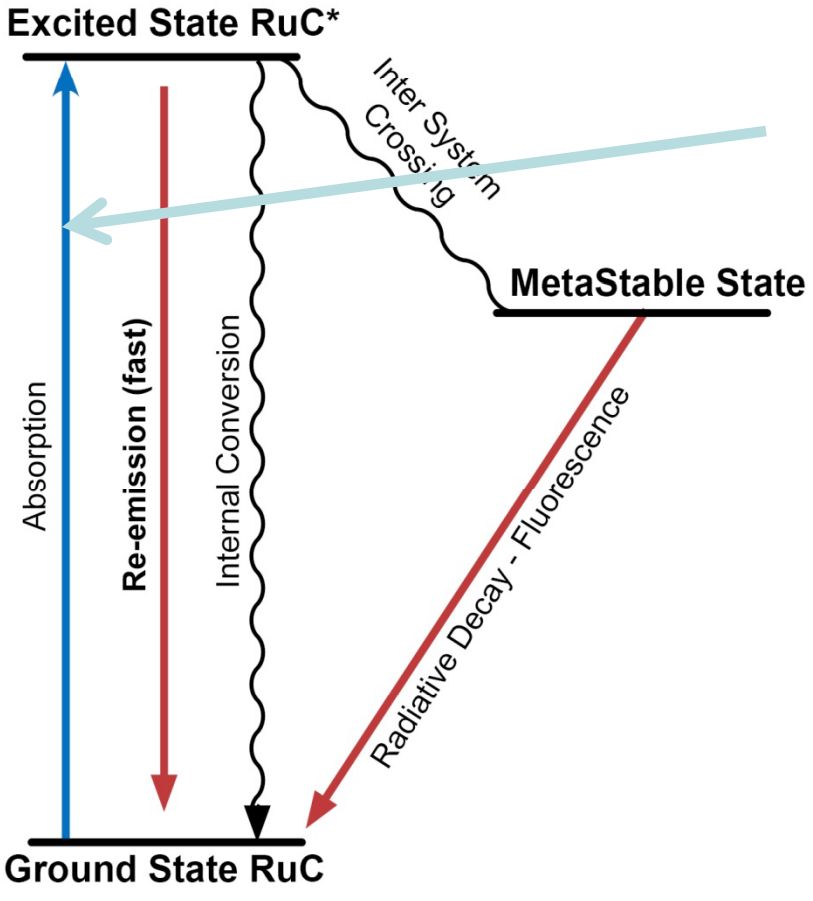
$$RuC^* \xrightarrow{\text{internal}} RuC$$

$$RuC^* \xrightarrow{\text{inter system}} RuC^{**}$$

$$RuC^{**} \xrightarrow{\text{fluorescence}} RuC + h\nu$$

$$RuC^{**} + O_2 \xrightarrow{\text{quenching}} RuC + O_2$$

Fluorescence by Ruthenium Complexes



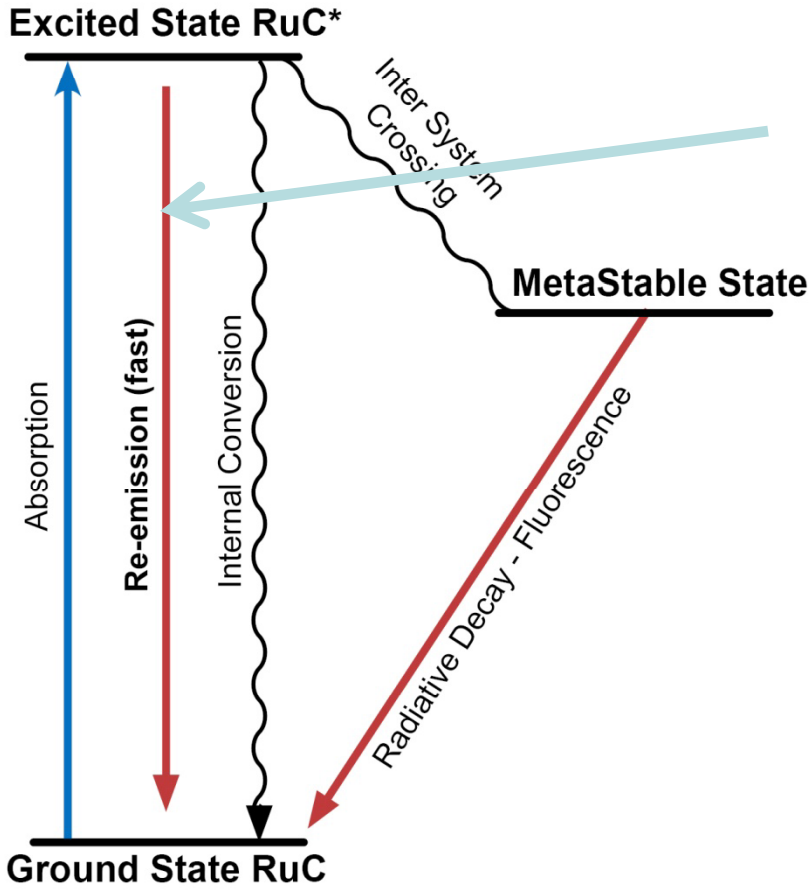
The Ruthenium complex absorbs a photon of blue light, which creates an excited state. This state is unstable, it has too much energy and so must find a way to get rid of the excess energy

$$RuC^* \xrightarrow{\text{inter system}} RuC^{**}$$

$$RuC^{**} \xrightarrow{\text{fluorescence}} RuC + h\nu$$

$$RuC^{**} + O_2 \xrightarrow{\text{quenching}} RuC + O_2$$

Fluorescence by Ruthenium Complexes



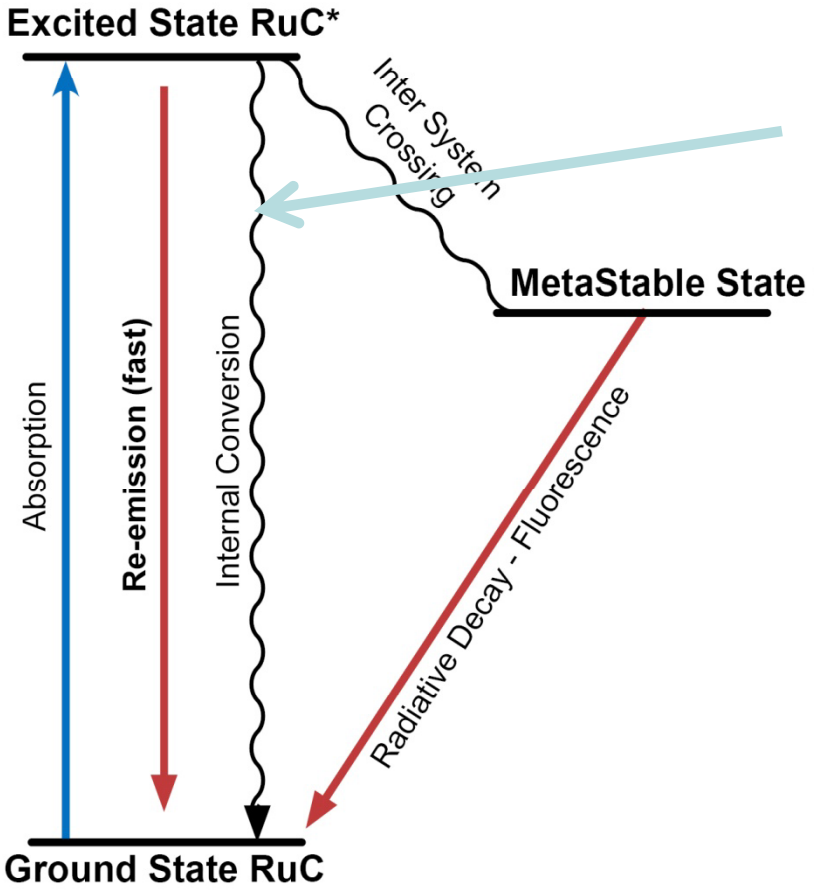
The complex may re-emit the photon, effectively acting as a light scatterer since the photon is emitted in random directions

$$RuC^{*} \xrightarrow{\text{inter system}} RuC^{**}$$

$$RuC^{**} \xrightarrow{\text{fluorescence}} RuC + h\nu$$

$$RuC^{**} + O_2 \xrightarrow{\text{quenching}} RuC + O_2$$

Fluorescence by Ruthenium Complexes



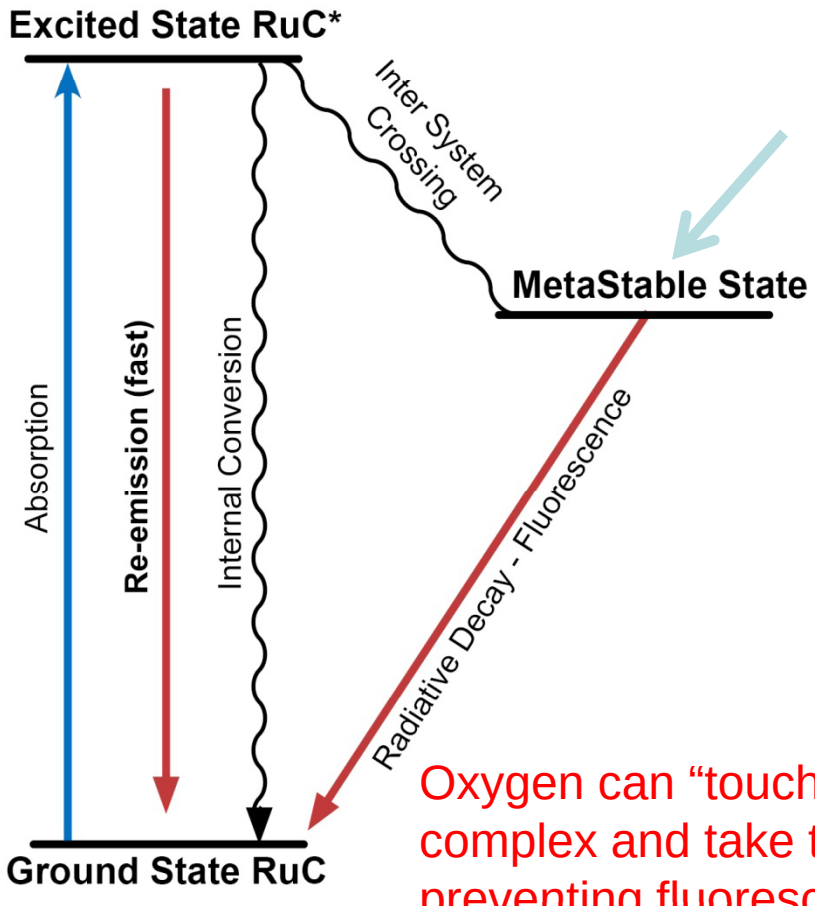
The complex may also get rid of the energy through a series of energy transfer reactions internally, converting the excess energy to vibrational or rotational energy

$$RuC^{*} \xrightarrow{\text{inter system}} RuC^{**}$$

$$RuC^{**} \xrightarrow{\text{fluorescence}} RuC + h\nu$$

$$RuC^{**} + O_2 \xrightarrow{\text{quenching}} RuC + O_2$$

Fluorescence by Ruthenium Complexes



During the energy loss process – the system my stop at an intermediate electronic level – a metastable state – where it can stay for a while – and then undergo radiative decay – this is the fluorescence we are looking for

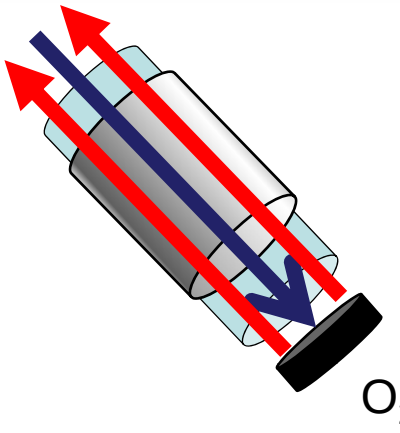
$$RuC^{**} \xrightarrow{\text{fluorescence}} RuC + h\nu$$

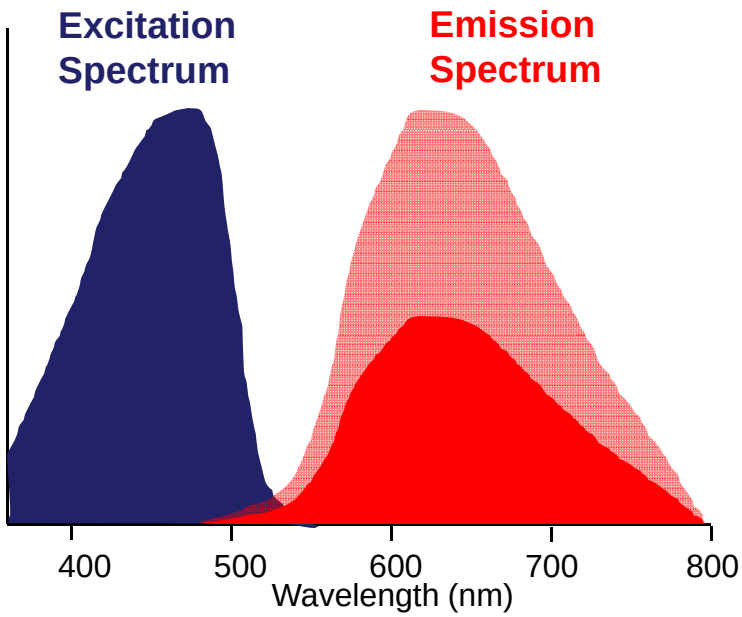
$$RuC^{**} + O_2 \xrightarrow{\text{quenching}} RuC + O_2$$

Oxygen can "touch" the metastable complex and take the energy away – preventing fluorescence

Excitation and Emission

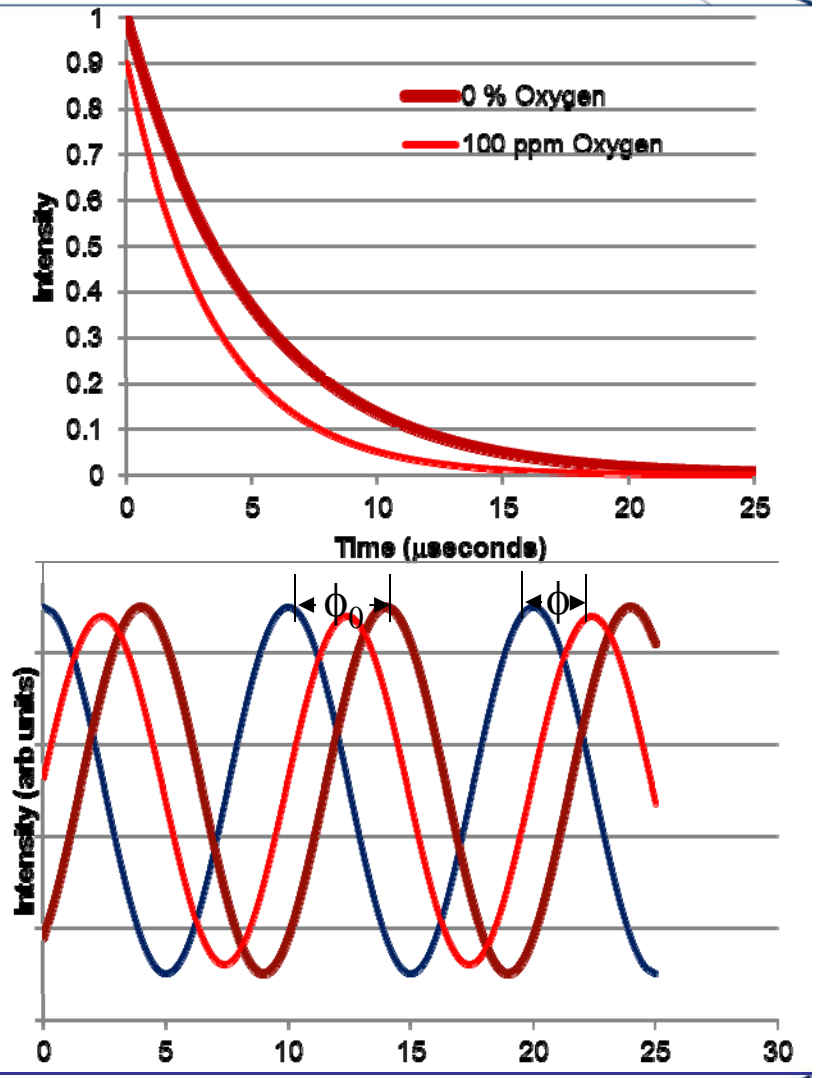
- A fiber optic is used for the measurement
- The ruthenium complex is coated at tip
- A blue LED shines down the fiber
- 475 nm – about the peak of excitation
- The RuC fluoresces in the red
- The photons from the fluorescence travel back up the fiber where they are detected
- Oxygen molecules in contact with the tip reduce the fluorescence signal – hence fluorescence quenching





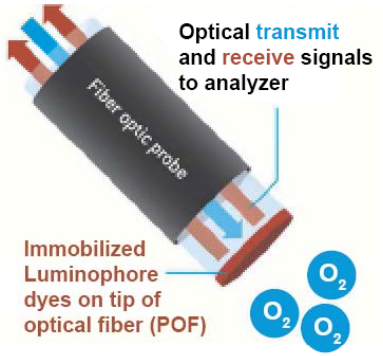
Intensity and Decay Time

- Excited state has a “lifetime” – takes a while to decay away
- Oxygen “quenches” and makes it decay faster
- If you AC modulate the **excitation**, **fluorescence** comes back at same frequency but phase shifted.
- If **oxygen** is present, the amount of phase shift decreases (like intensity)
- Both Phase change and Intensity change proportional to Oxygen concentration



And that is how it is done

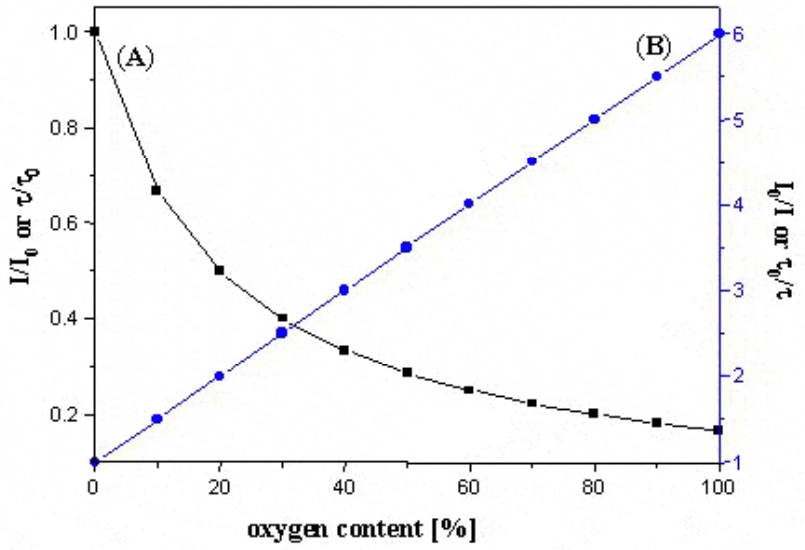
- Coat the end of a fiberoptic with the right material
- Excite it and measure the fluorescence intensity and phase shift in presence of O_2
- Changes are linearly related to oxygen concentration (Stern Volmer Equation)
- Make it into a probe and insert where needed



$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV} \cdot [O_2]$$

$$I = f([O_2])$$

$$\tau = f([O_2])$$



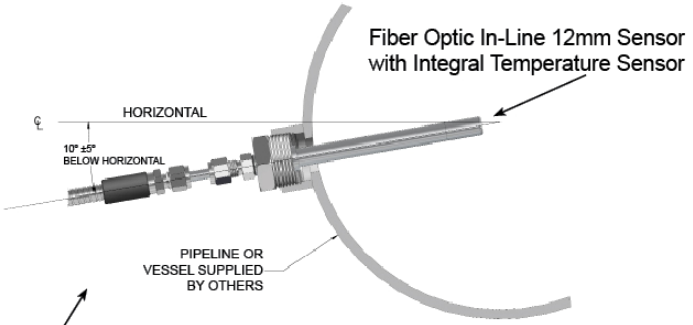
And that is how it is done

Analyzer/Controller

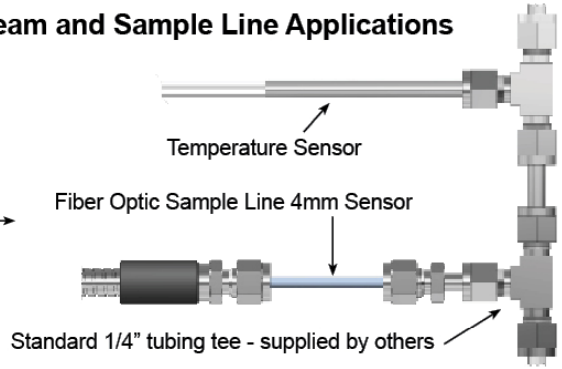


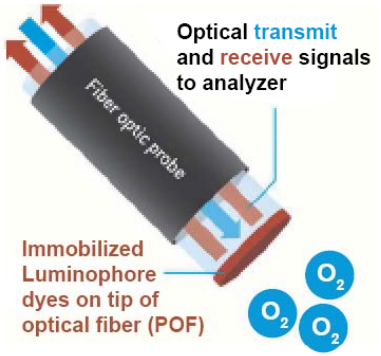
Works with all installation types and sensors.

Pipe and Vessel Installations



Slipstream and Sample Line Applications

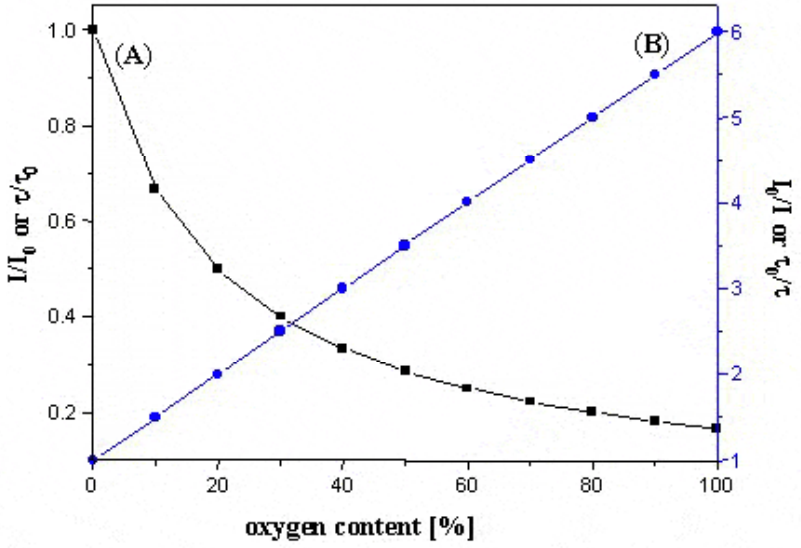




$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV} \cdot [O_2]$$

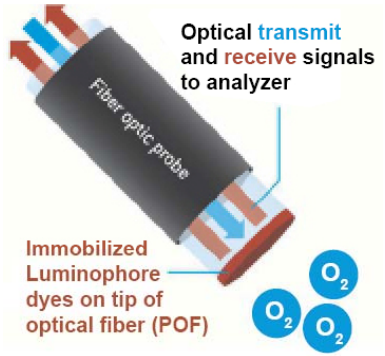
$$I = f([O_2])$$

$$\tau = f([O_2])$$



Capabilities

Optical Oxygen Probes



- High Accuracy [1 ppb (*aq*), <5 ppm (*g*)]
- Measurement is unaffected and independent of process sample flow rate
- Pressure up to 1500 psig
- No cross sensitivity or damage to sensor from CO_2, H_2S, SO_2, pH, S_2, SO_4^{2-}, Chloride, H_2, NO_2 or Pb.
- In-situ sensor requires no energy or heat and is suitable for installation into H_2, hydrocarbons or other applications where combustibles are present.
- Fast response [t_{90} , <6s (*g*), t_{90} , <40s (*aq*)]
- High stability (more than 100,000 data points without drift)
- Long exposure to inert gas. No "falling asleep" syndrome.

- Boiler Feedwater
- Water Re-injection wells
- Produced water/ condensates
- Natural gas / LNG
- Nitrogen Blanketing
- SRU startup
- Stack Gas
- Compressor suction leaks
- (insert your application here)

Natural Gas Pipelines

- Measurement of 0 to 100 ppm oxygen in natural gas, with no poisoning or interference from hydrogen sulfide or carbon dioxide.
- Low maintenance, resistant to poisoning, dewpoint upsets, and calibration drift free.
- Provides long-term protection in regards to oxygen induced corrosion

Stack Gas Analysis

- "Tough" application – SRU stack gas with high SO2 and ammonia



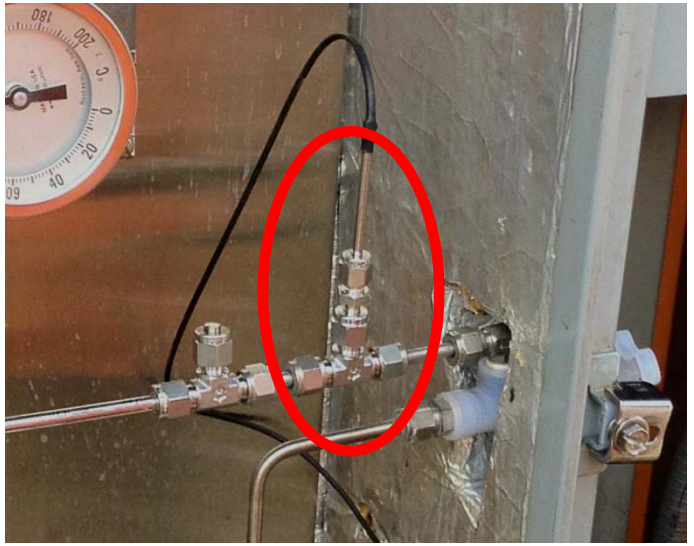
Stack Gas Analysis

- “Tough” application – SRU stack gas with high SO2 and ammonia
- Existing zirconia analyzer having plugging / corrosion issues



Stack Gas Analysis

- “Tough” application – SRU stack gas with high SO2 and ammonia
- Existing zirconia analyzer having plugging / corrosion issues
- Installed fiber-optic probe inside oven of stack gas SO2 analyzer



Stack Gas Analysis

- "Tough" application – SRU stack gas with high SO2 and ammonia
- Existing zirconia analyzer having plugging / corrosion issues
- Installed fiber-optic probe inside oven of stack gas SO2 analyzer
- Installed Class 1 Div 2 controller up on the stack as well



"The analyzer has far surpassed the expectations, and given the severe conditions. It is noteworthy since the mose significant difference is the ease of installation without the use of complex and expensive sample conditioning".

Concluding Remarks

- Phase Fluorimetry is a proven method of oxygen analysis
- The method is accurate and reliable even in harsh environments
- It can be used for gas phase applications from parts per millions to percent levels of oxygen
- In liquid applications, it can measure to 1 part per billion up to 22 part per million