What is Singlet Oxygen?
SINGLET OXYGEN GENERATION

\[ S_n \]
\[ S_m \]
\[ S_1 \]

\[ T_m \]

\[ T_1 \]

\[ S_0 \]

Two Photon

One Photon

\[ O_2(b^1\Sigma^+) \]

Absorption

Oxygenation and/or Oxidation of M

\[ O_2(a^1\Delta_g) \]

Phosphorescence

Energy Transfer

\[ O_2(X^3\Sigma_g^-) \]

Phosphorescence and Physical Deactivation
Singlet Oxygen Detection

1. Direct measurement of singlet oxygen luminescence (TCSPC)

2. Indirect measurement
   a) Germanium detector
   b) Chemical methods
\[ \text{O}_2(a^1\Delta_g) \rightarrow \text{O}_2(X^3\Sigma_g^-) \text{ produces phosphorescence signal at 1270 nm} \]
Singlet oxygen luminescence detected in air-equilibrated toluene after excitation at 550 nm for optically matched solutions of 2, 3, 6 and TPP in toluene.

- Sample is excited with frequency tripled Nd:YAG laser emitting at 355 nm.
- Luminescence collected and transferred to infrared sensitive photomultiplier equipped with a 1270 nm interference filter.
- Single photon counting setting enables time-resolved detection, while stop signal is provided by a photodiode (PD): via beam splitter (BS).
- Spectral resolution achieved either by different interference filters from 1100 to 1400 nm or by using a spectrometer (SP).

Singlet oxygen luminescence detected in air-equilibrated toluene after excitation at 550 nm for optically matched solutions of 2, 3, 6 and TPP in toluene.
Quantification

\[ I = \gamma \cdot k_r \cdot \tau_\Delta \cdot \Phi_\Delta \cdot (1 - 10^{-\text{OD}}) \cdot I_{\text{ex}} \]

\[ \Phi_\Delta = \frac{I}{I_{\text{ref}}} \cdot \Phi_{\Delta_{\text{ref}}} \]
Is it worth pursuing?

Advantages

• Signal is distinct and not mistaken even with solvent change.
• Luminescence from other species occurs at wavelengths lower than 1000 nm.
• Quick to get results.
• Little room for human error.

Disadvantages

• Signal is weak.
• Detectors in the detection region are not as sensitive as at lower wavelengths.
• Expensive specific special instrumentation required.
Singlet Oxygen Detector Setup

- Nd:YAG Laser
- dye laser
- beam splitter
- photo diode
- "Trigger"
- Oscilloscope
- "Signal"
- Ge-detector
- filter
- sample
How it works

• Singlet oxygen quenchers cause shortening of singlet oxygen lifetime.

• NaN₃ singlet oxygen specific quencher mainly used.

• Change in the lifetime is reflected in the change in the singlet oxygen depletion curve.
Quantification

\[ I(t) = B \frac{\tau_D}{\tau_T - \tau_D} \left[ e^{-t/\tau_T} - e^{-t/\tau_D} \right] \]

\( I(t) \) = phosphorescence intensity of \( ^1O_2 \) at time \( t \)

\( \tau_D \) = lifetime of \(^1O_2\) phosphorescence decay

\( \tau_T \) = triplet state lifetime of the standard or sample

\( B \) = coefficient involved in sensitizer concentration and \(^1O_2\) quantum yield.
Is it worth pursuing?

Advantages
• Quick to get results.
• Little room for human error.
• Not laborious.
• Note dependent on the exact phosphorescence intensity.

Disadvantages
• Expensive special instrumentation required.
CHEMICAL METHODS

• Uses fluorescent scavenging/trap molecules whose optical properties (absorbance/fluorescence) change with singlet oxygen interaction.

• Common trap molecules are diene molecules capable of $\pi_2 + \pi_4$ cycloaddition to yield endoperoxides.

\[
\text{DPBF} + ^1\text{O}_2 \rightarrow \text{DDEBD} \rightarrow \text{DBB}
\]

DPBF = 1,3-diphenylisobenzofuran
DDEBD = 1,4-diphenyl-1,4-dihydro-1,4-epoxybenzo[6][1,2]dioxine
DBB = 1,2-phenylenebis(phenylmethanone)
More complex systems

Chemical structures showing the transition from a non-fluorescent to a fluorescent state.
Observations

- Fluorescence or absorption spectra change with time proportional to the singlet oxygen present.
Quantification

\[
\frac{1}{\Phi_{\text{DPBF}}} = \frac{1}{\Phi_\Delta} + \frac{1}{\Phi_\Delta} \frac{k_d}{k_a} \frac{1}{[\text{DPBF}]}
\]

- \(\Phi_\Delta\) is obtained from the plot of \(1/\Phi_{\text{DPBF}}\) versus \(1/[\text{DPBF}]\)

\[
\Phi_\Delta = \Phi_{\text{std}} \cdot \frac{R \cdot I_{\text{std}}}{R_{\text{std}} \cdot I_{\text{abs}}}
\]
Is it worth pursuing?

Advantages
• Less specialized equipment required.
• No fittings required.
• Can detect generation of small amounts of singlet oxygen.
• Detected signals in high detector efficiency wavelengths.

Disadvantages
• Time consuming depending on sample and quencher.
• Laborious
• A lot of room for human error.
SUMMARY

- Singlet oxygen is produced from different processes but significantly from the triplet excited state of a photosensitizer to triplet molecular oxygen.

- All detection methods detect singlet oxygen regardless of its source.

- For quantification purposes a reference standard is usually required.
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