OXYTEC TR - Measurement Principle of optical oxygen-sensitive sensor

1. Dynamic Quenching of Luminescence

The principle of measurement is based on the effect of dynamic luminescence quenching by molecular oxygen. The following scheme explains the principle.

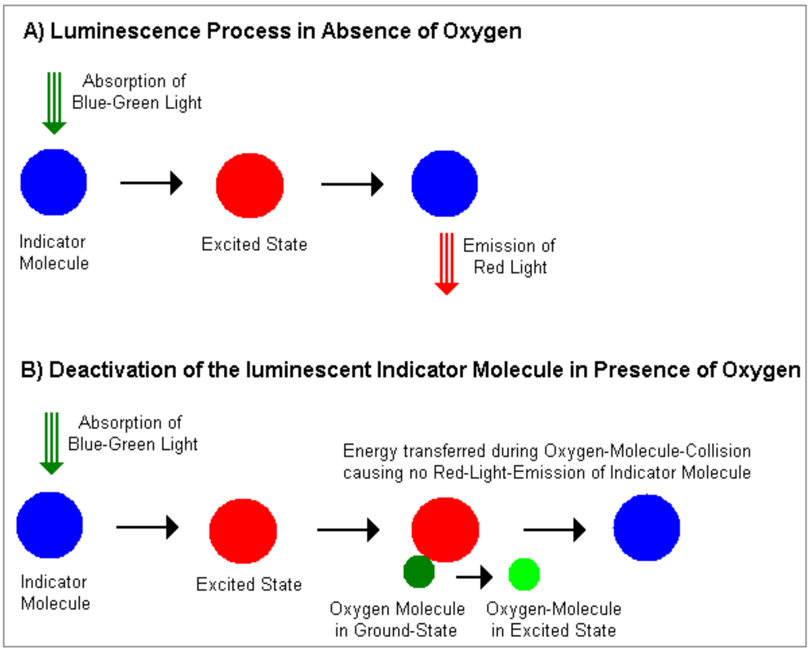

***Figure 1** Principle of dynamic quenching of luminescence by molecular oxygen*

The collision between the luminophore (indicator molecule) in its excited state and the quencher (oxygen) results in radiationless deactivation and is called collisional or dynamic quenching. After collision, energy transfer takes place from the excited indicator molecule to oxygen which consequently is transferred from its ground state (triplet state) to its excited singlet state. As a result, the indicator molecule does not emit luminescence and the measurable luminescence signal decreases.

A relation exists between the oxygen concentration in the sample and the luminescence intensity as well as the luminescence lifetime which is described in the Stern-Volmer-equation (**1**). Here, τ_0 and τ are the luminescence decay times in absence and presence of oxygen (I_0 and I are the respective luminescence intensities), $[O_2]$ the oxygen concentration and K_{SV} the overall quenching constant.

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV} \cdot [O_2]$$
$$I = f([O_2]) \qquad (\mathbf{1})$$
$$\tau = f([O_2])$$

- I: Luminescence intensity in presence of oxygen
- I_0: Luminescence intensity in absence of oxygen
- τ: Luminescence decay time in presence of oxygen
- τ_0: Luminescence decay time in absence of oxygen
- K_{SV}: Stern-Volmer constant (quantifies the quenching efficiency and therefore the sensitivity of the sensor)
- $[O_2]$: Oxygen content

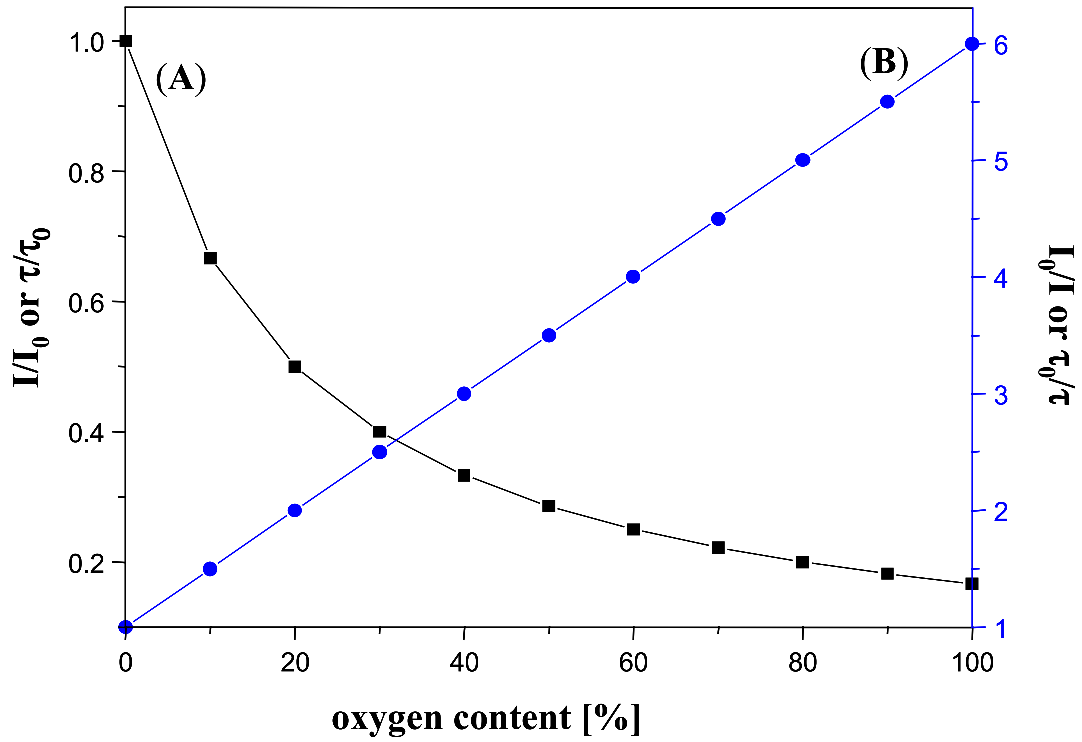

***Figure 2** (**A**) Luminescence decrease in the presence of oxygen. (**B**) Stern-Volmer plot.*

Indicator dyes quenched by oxygen are, for example, polycyclic aromatic hydrocarbons, transition metal complexes of Ru(II), Os(II) and Rh(II), and phosphorescent porphyrins containing Pt(II) or Pd(II) as the central atom.

2. Luminescence Decay Time

The Oxytec TR measures the luminescence decay time of the immobilized luminophore as the oxygen-dependent parameter.

$$\tau = f([O_2]) \quad (2)$$

The Oxytec TR uses the phase modulation technique to evaluate the luminescence decay time of the indicators. If the luminophore is excited with light with sinusoidally modulated intensity, its decay time causes a time delay in the emitted light signal. In technical terms, this delay is the phase angle between the exciting and emitted signal. This phase angle is shifted as a function of the oxygen concentration. The relation between decay time τ and the phase angle Φ is shown by the following equation:

$$\tau = \frac{\tan\Phi}{2\pi \cdot f_{mod}} \quad (3a)$$

$$\tan\Phi = 2\pi \cdot f_{mod} \cdot \tau \quad (3b)$$

$$\tau \equiv \tan\Phi \equiv \Phi \equiv f([O_2]) \quad (3c)$$

τ: luminescence decay time; Φ: phase angle; f_{mod}: modulation frequency

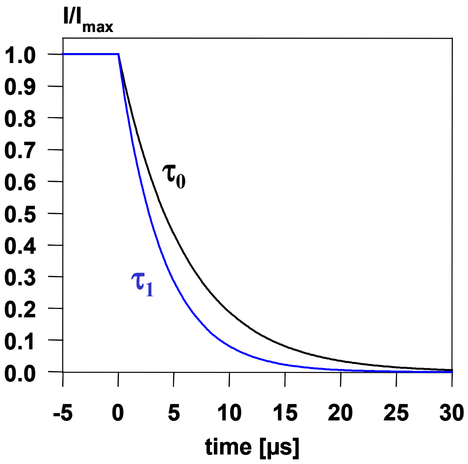

Figure 5 *Schematic of the single exponential decay (t_0 > t_1).*

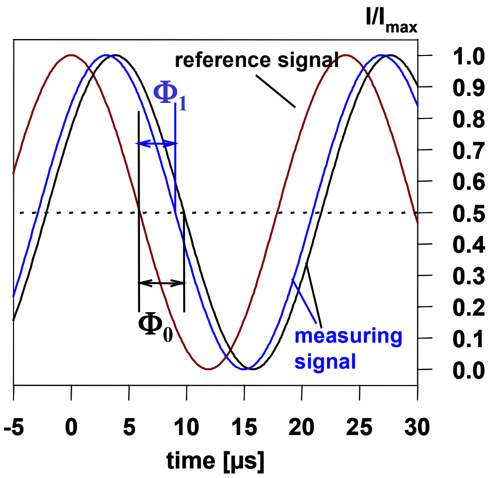

Figure 6 *The luminophore is excited with sinusoidally modulated light. Emission is delayed in phase expressed by the phase angle F relative to the excitation signal, caused by the decay time of the excited state*

The Oxytec TR measurement of the luminescence decay time, an intrinsically referenced parameter, has the following advantages compared to the conventional intensity measurement:

- The decay time does not depend on fluctuations in the intensity of the light source and the sensitivity of the detector;
- The decay time is not influenced by signal loss caused by fiber bending or by intensity changes caused by changes in the geometry of the sensor;
- The decay time is, to a great extent, independent of the concentration of the indicator in the sensitive layer ➔ photo bleaching and leaching of the indicator dye has no influence on the measuring signal;
- The decay time is not influenced by variations in the optical properties of the sample including turbidity, refractive index and coloration.

3. Major Components of the Fiber-Optic Sensor Oxytec TR

In the sensor, the product or sample to be measured interacts generally with an indicator layer and changes its optical properties. The result is either a change in the color (absorbance or spectral distribution) or the luminescence properties (intensity, lifetime, polarization). Light acts as the carrier of the information. The major components of a typical fiber-optical sensing system are:

- a light source to illuminate the sensor (laser, light emitting diode, lamps)
- an optical fiber as signal transducer (glass fiber)
- a photo detector (photodiode, photomultiplier tube, CCD-array)
- the optical sensor (indicator immobilized in a solid matrix)

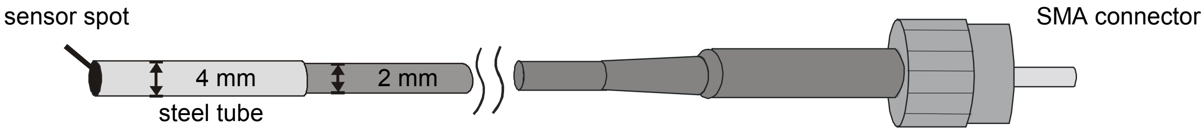

Figure 3 *Scheme of an optical fiber*

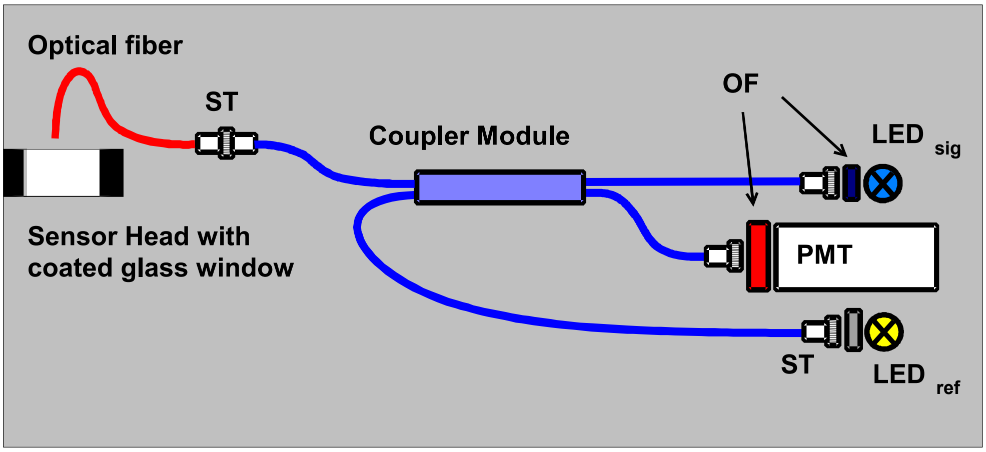

Figure 4 *Oxytec TR - Schematic drawing of the optical setup of the measuring system (LED: light emitting diodes, PMT: photomultiplier, OF: optical filters, ST: fiber connector).*

4. Advantages of Optical Oxygen-Sensitive Sensor Oxytec TR

- faster response time –> savings on product loss;
- not sensitive to pressure shocks (system without membrane);
- no electrolyte has be changed/renewed (system without electrolyte);
- no oxygen is consumed during the measurement;
- easy to maintain –> no exchange of membranes or electrolyte and no polarization time required;
- the signal is independent of changes in flow velocity;
- is able to measure the oxygen content in dry gases;
- is insensible towards electrical interferences and magnetic fields;
- is more sensitive than conventional electrodes (up to low ppt-range);
- long-term stability and low drift;
- light-conducting fibers are able to transport more information than power currents (information can be simultaneously transferred, e.g. intensity of light, spectral distribution, polarization, information such as decay time or delayed fluorescence).

5. Technical Data of Oxytec TR

Measuring range:	I) 1 ppb – 2 ppm or II) 20 ppb – 40 ppm
Repeatability:	+/- 1% (+/-1 ppb for I or +/-20 ppb for II)
Response time:	t90 = 25 s
Temperature compensation:	Pt100
Temperature range:	-5°C - +50°C (+23°F - +122°F)
Temperature resistance:	max. 130 °C (max. 266 °F)
Pressure range:	max. 12 bar
Process connection:	compatible to Varivent©-inline-housings DN 40 (1,5“) – DN 150 (6“)
Input:	6x digital (24 VDC)
Output:	3x digital (24 VDC), 2x analog (4-20 mA)
Enclosure rating:	IP 65
Power Supply:	24 VDC

6. Front- and Back view of the compact Oxytec TR

- Front view with Display and keypad

- Back view with sensor head (Varivent®-compatible) and optical window spot