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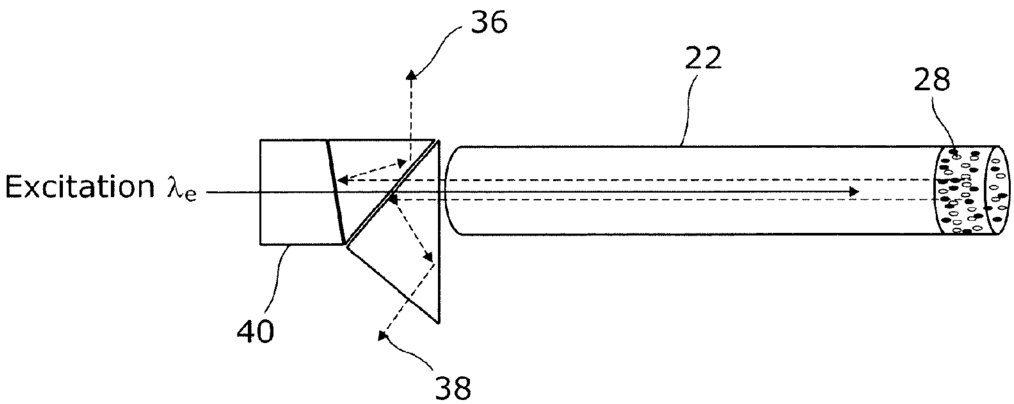
(54) Titre : CAPTEUR D'OXYGENE COMPRENANT UNE FIBRE OPTIQUE DE GRAND DIAMETRE A POINTE REVETUE
(54) Title: OXYGEN SENSOR COMPRISING A TIP COATED OPTICAL FIBRE WITH A LARGE DIAMETER



(57) **Abrégé/Abstract:**
The invention relates to an oxygen sensor including an oxygen sensitive fluorescent material which reduces or removes the possibility of the oxygen concentration being misinterpreted.

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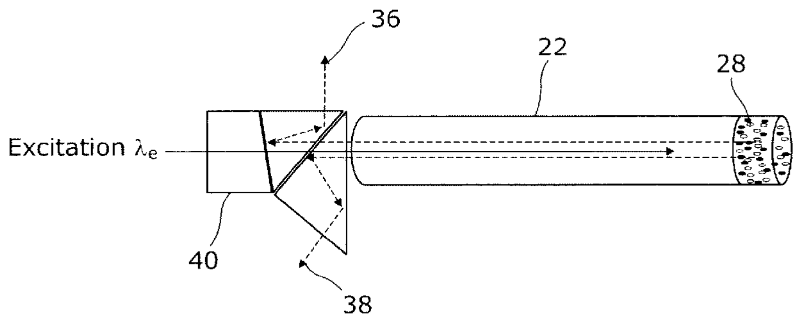

Figure 2

(57) Abstract: The invention relates to an oxygen sensor including an oxygen sensitive fluorescent material which reduces or removes the possibility of the oxygen concentration being misinterpreted.

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OXYGEN SENSOR COMPRISING A TIP COATED OPTICAL FIBRE WITH A LARGE DIAMETER

The present invention relates to an oxygen sensor and more particularly to an oxygen sensor for use in aircraft applications, more in particular fuel tank or air separation module applications.

The present invention provides an improvement in measuring the concentration of oxygen. This invention will be of particular use in measuring oxygen concentration in aircraft fuel tank ullage or air separation modules.

It is known to use fluorescent quenching to indicate the presence of certain species of interest. A fluorescent material emits a specific wavelength and intensity of light which has a specific emission lifetime, upon excitation by a specific wavelength which is lower than the emitted wavelength. The intensity and lifetime of the emission is dependent upon the concentration of oxygen in contact with the fluorescent material. As the oxygen concentration increases the fluorescent emission intensity and lifetime decreases and the increase and decrease are directly proportional to one another.

Sensors used inside fuel tanks consist of a fluorescent material surface which is exposed to the fuel tank environment. A reduction in the fluorescent material's emission intensity and lifetime in the presence of oxygen gives a direct measure of oxygen concentration around the sensor surface. The fluorescent emission of a material that is electromagnetically excited decreases in direct proportion to the concentration of a species of interest. Materials such as platinum tetrakis pentafluorophenyl porphyrin and platinum octaethylporphyrin are used as gaseous oxygen sensing materials. However, the fuel tank environment is harsh and can cause the fluorescent material to degrade. This degradation of the material will result in a reduction in the intensity and changes in lifetime of fluorescent emission and this can be incorrectly interpreted as a higher oxygen level.

The process of fluorescence emission can be summarised as follows:

Excitation: $L + hv1 = L^*$ (equation 1)

Fluorescence: $L^* = L + hv2$ (equation 2)

Quenching: $L^* + O_2 = L + O_2^*$ (equation 3)

Equation 1 shows the process of electromagnetic excitation of a fluorophore by a photon with energy $hv1$. Equation 2 shows the emission of a photon at energy $hv2$ when the excited fluorophore L^* returns to the de-excited state L and wherein $hv2 < hv1$. In the presence of oxygen, the fluorophore transfers energy to the oxygen molecule through collision as is shown by Equation 3. This energy transfer does not release a photon in a process that is defined as quenching. The quenching of the excited fluorophore by an oxygen molecule results in the decrease of total intensity and lifetime of emission. It is this mechanism that has allowed an optical oxygen sensor to be developed. The sensors have found particular utility in aerospace fuel tanks but it has been found that when the sensor is exposed to liquid fuel the oxygen sensitive material degrades. Also, as the fluorescent material is exposed to fuel in a tank, the fluorophore can be masked by the hydrocarbon molecules in the fuel. This interaction can result in photo-bleaching which can result in an irreversible degradation of the fluorophore. If the fluorophore and oxygen do not interact then the overall emission intensity and lifetime increases. This increase can be incorrectly interpreted as a lower oxygen concentration. It will also be necessary to calibrate or reference the emission from the oxygen sensitive fluorophore.

The present invention seeks to overcome the problems of the prior art by providing an oxygen sensor including an oxygen sensitive fluorescent material including a combination of: an oxygen sensitive dye and an oxygen insensitive dye, wherein both of the dyes are fluorophores. The oxygen insensitive dye could be silicon octaethylporphyrin. The oxygen sensitive dye could be platinum tetrakis pentafluorophenylporphyrin or platinum octaethylporphyrin. The two dyes can be dispersed in a polymer matrix, for example polydimethyl siloxane. Alternatively the material can be made using sol-gel xerogel process. Using this technique it is possible to disperse the material in a fuel resistant and oxygen permeable fluorosilicone rubber.

The oxygen sensitive dye and the oxygen insensitive dye can be excited at the same wavelength. Each of the dyes emits a different wavelength, intensity and lifetime to the other. Upon interaction with oxygen molecules the emission intensity and lifetime is reduced for the oxygen sensitive dye whilst that of the oxygen insensitive dye remains unchanged.

The sensor has a tip comprising of the combination of the oxygen insensitive dye and oxygen sensitive dye. The tip is at an end of a large optical diameter fibre. The other end of the large optical diameter fibre is connectable to a prism or sensors to separate the wavelengths. The large diameter fibre is housed in a tube, preferably made of steel. One end of the tube has a rubber membrane and one or more breather vents that prevent the liquid fuel from contacting the fluorophores but which do permit interaction between the fluorophores and oxygen. The membrane can be made of any suitable material which is resistant to aerospace fuel and which is permeable to gaseous oxygen, such as fluorosilicone rubber, polydimethyl siloxane.

An apparatus for transmitting the excitation light and to pick up the emissions from the oxygen sensitive fluorescent material includes an optical fibre. This fibre is preferably of a large diameter. The apparatus further includes a trichroic prism and two photodetectors or tricolour sensors such as integrated RGB sensors. The trichroic prism and two photodetectors or tricolour sensors such as integrated RGB sensors separate the three wavelengths; excitation, and the emission from each dye. The intensity or lifetime is converted into proportional currents. Transimpedance amplifiers are used to convert the currents into a voltage (V1) which is proportional to the intensity or lifetime of the emission from the oxygen insensitive dye and a voltage (V2) which is proportional to the intensity or lifetime of the emission from the oxygen sensitive dye. The excitation is pulsed in order to measure the lifetime of the emission. Typically, the fluorescent lifetime is between 70 and 100μs and is monitored for a known time. It is possible to measure both the lifetime and the intensity together.

During operation of the sensor, the voltages (V1 and V2) are compared with each other to infer the performance of the oxygen sensitive fluorescent material. As the oxygen level increases, V2 decreases and V1 remains unchanged. If the material degrades with no change in the oxygen concentration then V1 and V2 will decrease together. The material's performance, oxygen concentration and sensitivity can be calibrated by the ratio of V1/V2. This comparison of voltages is effectively an in-built self-check.

The invention will now be described with reference to the accompanying figures in which:

Figure 1 shows a sensor probe having a sensor according to the present invention.
Figure 2 shows a sensor and a means for separating the wavelengths of emissions from the fluorophores and excitation according to the present invention.
Figure 3 shows an example of the fluorescent emission from two fluorophores.
Figure 4 shows a window of known time in which to measure the lifetime of an emission.

Figure 1 shows a sensor probe 20 which includes a large diameter fibre 22 having a fibre connector 24 to connect the fibre to a trichroic prism or tricolour sensor. The large diameter fibre 22 has a tip 26 (shown in more detail in the exploded section) which terminates in an oxygen sensitive fluorescent material 28 which includes an oxygen sensitive dye and an oxygen insensitive dye wherein the dyes are both fluorophores. The large diameter fibre 22 is placed inside a tube 30 for protection. The tube has a breather vent 32 attachable thereto which includes a membrane to prevent liquid fuel from contacting the dual fluorophore tip 28.

Figure 2 shows a simplified version of the sensor probe shown in figure 1. The oxygen sensitive fluorescent material 28 is located at one end of the large diameter optical fibre 22. At the other end of the optical fibre 22 is a trichroic prism 40. Photons are sent through the prism 40 and are transmitted by the optical fibre 22 to excite the fluorophores in the tip 28. The emissions from the fluorophores are transmitted by the fibre 22 and are passed through a trichroic prism 40 to separate the three wavelengths made up of the excitation, the emission from the oxygen sensitive dye 36 and the oxygen insensitive dye 38. Two photodetectors (not shown) are used to convert the intensity or lifetime information into proportional currents I1 and I2. The current is then converted into voltage by transimpedance amplifiers.

Figure 3 shows a graph of energy against fluorescence intensity. It can be seen that the intensity of the emission from the oxygen sensitive dye decreases and the oxygen concentration increases. However, the intensity of the emission from the oxygen insensitive dye remains unaffected by the change in oxygen concentration.

Figure 4 shows a measurement window 50 of a known time in which the emission lifetime is measured. The total integrated intensity in the measurement window 50 gives a measurement of the oxygen concentration.

Same design of oxygen sensor as described and shown can be used for fuel tank as well as air separation module applications.

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or in a method for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

Claims:

1. An apparatus for measuring the oxygen concentration in an aircraft fuel tank application or an aircraft air separation module application, the apparatus comprising:

   an oxygen sensitive fluorescent material (28) including a combination of: an oxygen sensitive dye and an oxygen insensitive dye, wherein both of the dyes are fluorophores;

   a large diameter optical fibre (22), the fibre having two ends (24, 26), to transmit photons and transmit emissions from the excited fluorophores, wherein the fluorescent material is located on an end (26) of the large diameter optical fibre (22);

   an excitation source, wherein the photons from the excitation source are transmitted by the large diameter optical fibre (22) to excite the fluorophores; and

   a trichroic prism (40) and two photodetectors, wherein the trichroic prism (40) and two photodetectors are configured to separate the three wavelengths made up of the excitation and the emission from each dye, wherein the excitation is pulsed to measure the lifetime of the emission.

2. The apparatus according to claim 1, wherein the large diameter optical fibre (22) is housed in a tube (30).

3. The apparatus according to claim 2, wherein the tube (30) has two ends, one of which has a rubber membrane and one or more breather vents (32) attachable thereto.

4. The apparatus according to claim 3, wherein the rubber membrane is resistant to aerospace fuel and is permeable to gaseous oxygen.

5. The apparatus according to any one of claims 1 to 4 wherein the oxygen sensitive dye is excitable at the same wavelength as the oxygen insensitive dye.

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6. The apparatus according to any one of claims 1 to 5 wherein the oxygen sensitive dye and oxygen insensitive dye are dispersed in a fuel resistant, oxygen-permeable rubber.

7. The apparatus according to claim 6 wherein the rubber is fluorosilicone rubber.

8. The apparatus according to any one of claims 1 to 7 wherein the intensity or lifetime of the fluorescence emitted by the excited fluorophores is converted into proportional currents and which are converted into voltages.

9. The apparatus according to claim 8 wherein transimpedance amplifiers are used to convert the currents into voltages.

10. A method of using an apparatus for measuring the oxygen concentration in an aircraft fuel tank application or an aircraft air separation module application, the apparatus comprising

an oxygen sensitive fluorescent material (28) including a combination of: an oxygen sensitive dye and an oxygen insensitive dye, wherein both of the dyes are fluorophores;

a large diameter optical fibre (22), the fibre having two ends (24, 26), to transmit photons and transmit emissions from the excited fluorophores, wherein the fluorescent material is located on an end (26) of the large diameter optical fibre (22);

an excitation source, wherein the photons from the excitation source are transmitted by the large diameter optical fibre (22) to excite the fluorophores; and

a trichroic prism (40) and two photodetectors, wherein the trichroic prism (40) and two photodetectors are configured to separate the three wavelengths made up of the excitation and the emission from each dye,

wherein the intensity or lifetime of the fluorescence emitted by the excited fluorophores is converted into proportional currents and which are converted into voltages; and

the method comprising:

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comparing the voltages to one another to infer the performance of the oxygen sensitive fluorescent material, wherein the excitation is pulsed to measure the lifetime of the emission.

11. The method according to claim 10, wherein the large diameter optical fibre (22) is housed in a tube (30).

12. The method according to claim 11, wherein the tube (30) has two ends, one of which has a rubber membrane and one or more breather vents (32) attachable thereto.

13. The method according to claim 12, wherein the rubber membrane is resistant to aerospace fuel and is permeable to gaseous oxygen.

14. The method according to any one of claims 10 to 13 wherein the oxygen sensitive dye is excitable at the same wavelength as the oxygen insensitive dye.

15. The method according to any one of claims 10 to 14 wherein the oxygen sensitive dye and oxygen insensitive dye are dispersed in a fuel resistant, oxygen-permeable rubber.

16. The method according to claim 15 wherein the rubber is fluorosilicone rubber.

17. The method according to any one of claims 10 to 16, wherein transimpedance amplifiers are used to convert the currents into voltages.

18. An apparatus for measuring the oxygen concentration in an aircraft fuel tank application or an aircraft air separation module application, the apparatus comprising:

an oxygen sensitive fluorescent material (28) including a combination of: an oxygen sensitive dye and an oxygen insensitive dye, wherein both of the dyes are fluorophores;

a large diameter optical fibre (22), the fibre having two ends (24, 26), to transmit photons and transmit emissions from the excited fluorophores, wherein

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the fluorescent material is located on an end (26) of the large diameter optical fibre (22);

an excitation source, wherein the photons from the excitation source are transmitted by the large diameter optical fibre (22) to excite the fluorophores; and

a tricolour sensor, wherein the tricolour sensor is configured to separate the three wavelengths made up of the excitation and the emission from each dye, wherein the excitation is pulsed to measure the lifetime of the emission.

19. The apparatus according to claim 18, wherein the large diameter optical fibre (22) is housed in a tube (30).

20. The apparatus according to claim 19, wherein the tube (30) has two ends, one of which has a rubber membrane and one or more breather vents (32) attachable thereto.

21. The apparatus according to claim 20, wherein the rubber membrane is resistant to aerospace fuel and is permeable to gaseous oxygen.

22. The apparatus according to any one of claims 18 to 21 wherein the oxygen sensitive dye is excitable at the same wavelength as the oxygen insensitive dye.

23. The apparatus according to any one of claims 18 to 22 wherein the oxygen sensitive dye and oxygen insensitive dye are dispersed in a fuel resistant, oxygen-permeable rubber.

24. The apparatus according to claim 23 wherein the rubber is fluorosilicone rubber.

25. The apparatus according to any one of claims 18 to 24 wherein the tricolour sensor is an integrated RGB.

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26. The apparatus according to any one of claims 18 to 25 wherein the intensity or lifetime of the fluorescence emitted by the excited fluorophores is converted into proportional currents and which are converted into voltages.

27. The apparatus according to claim 26 wherein transimpedance amplifiers are used to convert the currents into voltages.

28. A method of using an apparatus for measuring the oxygen concentration in an aircraft fuel tank application or an aircraft air separation module application, the apparatus comprising

an oxygen sensitive fluorescent material (28) including a combination of: an oxygen sensitive dye and an oxygen insensitive dye, wherein both of the dyes are fluorophores;

a large diameter optical fibre (22), the fibre having two ends (24, 26), to transmit photons and transmit emissions from the excited fluorophores, wherein the fluorescent material is located on an end (26) of the large diameter optical fibre (22);

an excitation source, wherein the photons from the excitation source are transmitted by the large diameter optical fibre (22) to excite the fluorophores; and

a tricolour sensor, wherein the tricolour sensor are configured to separate the three wavelengths made up of the excitation and the emission from each dye,

wherein the intensity or lifetime of the fluorescence emitted by the excited fluorophores is converted into proportional currents and which are converted into voltages; and

the method comprising:

comparing the voltages to one another to infer the performance of the oxygen sensitive fluorescent material, wherein the excitation is pulsed to measure the lifetime of the emission.

29. The method according to claim 28, wherein the large diameter optical fibre (22) is housed in a tube (30).

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30. The method according to claim 29, wherein the tube (30) has two ends, one of which has a rubber membrane and one or more breather vents (32) attachable thereto.

31. The method according to claim 30, wherein the rubber membrane is resistant to aerospace fuel and is permeable to gaseous oxygen.

32. The method according to any one of claims 28 to 31 wherein the oxygen sensitive dye is excitable at the same wavelength as the oxygen insensitive dye.

33. The method according to any one of claims 28 to 32 wherein the oxygen sensitive dye and oxygen insensitive dye are dispersed in a fuel resistant, oxygen-permeable rubber.

34. The method according to claim 33 wherein the rubber is fluorosilicone rubber.

35. The method according to any one of claims 28 to 34 wherein the tricolour sensor is an integrated RGB.

36. The method according to any one of claims 28 to 35, wherein transimpedance amplifiers are used to convert the currents into voltages.

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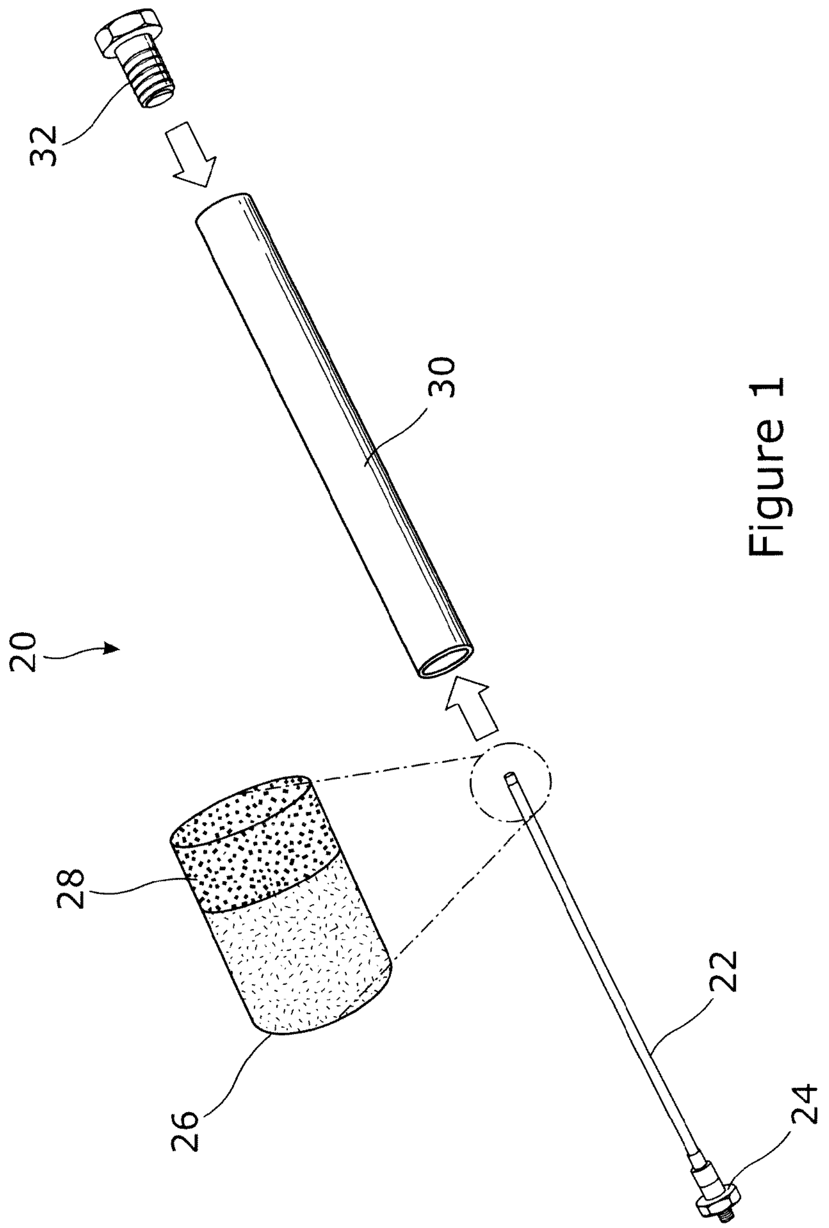


Figure 1

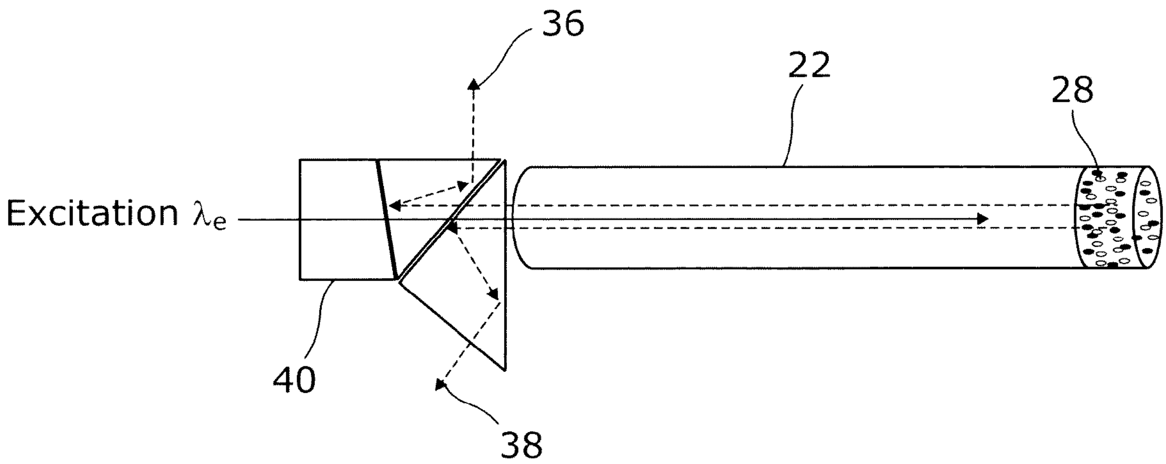


Figure 2

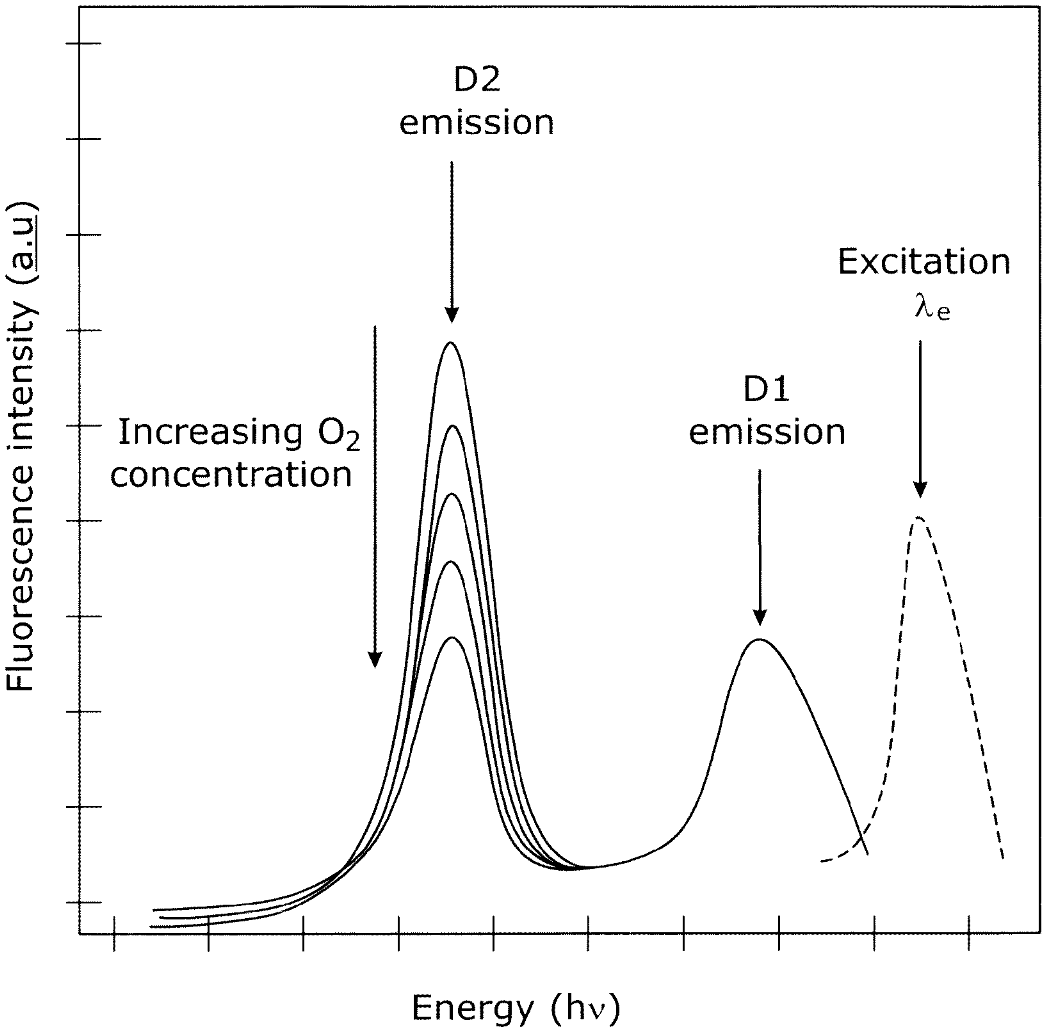

D2
emission
Excitation
λ_e
Increasing O_2
concentration
D1
emission
Fluorescence intensity (a.u)
Energy (hν)

Figure 3

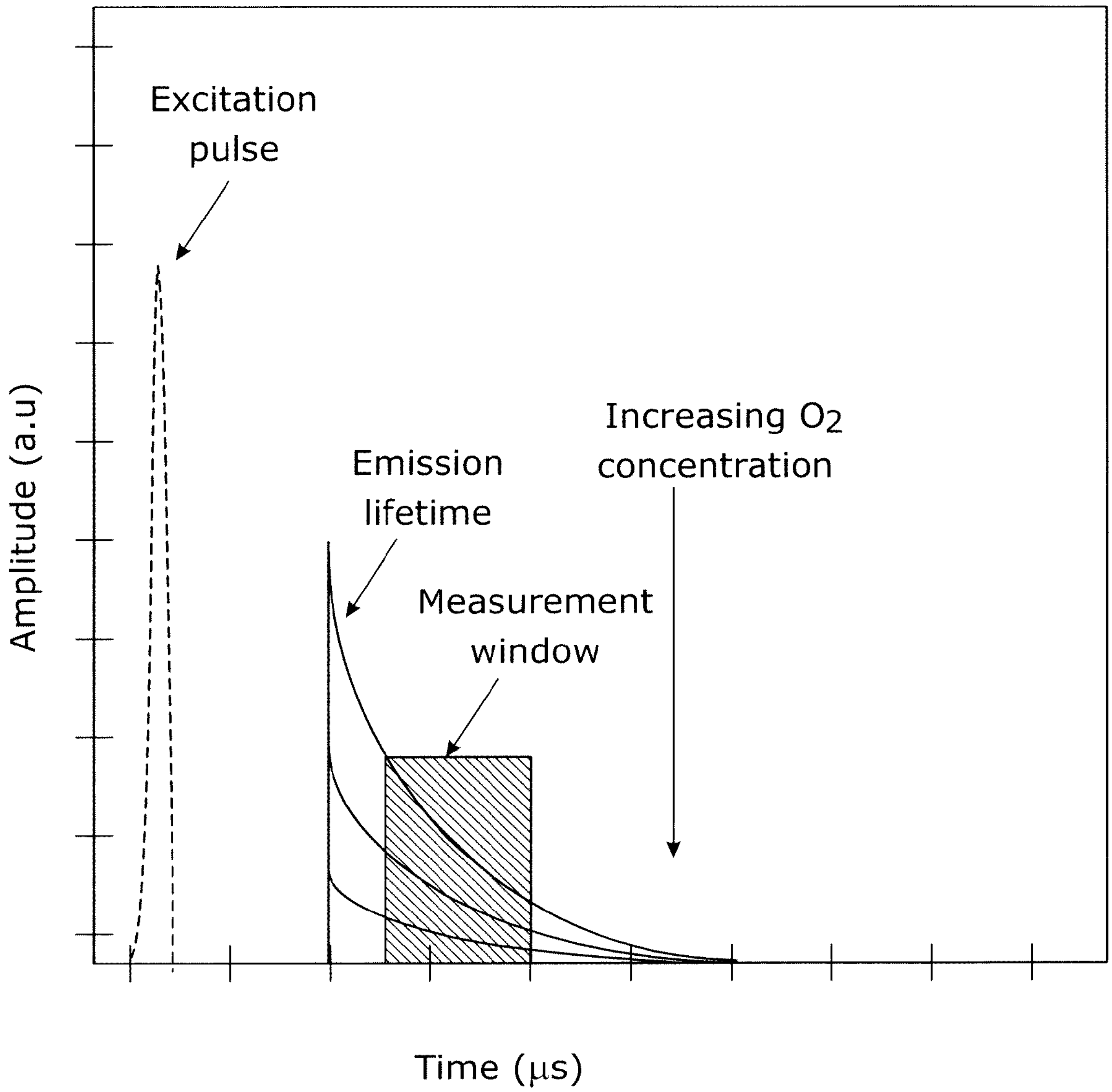
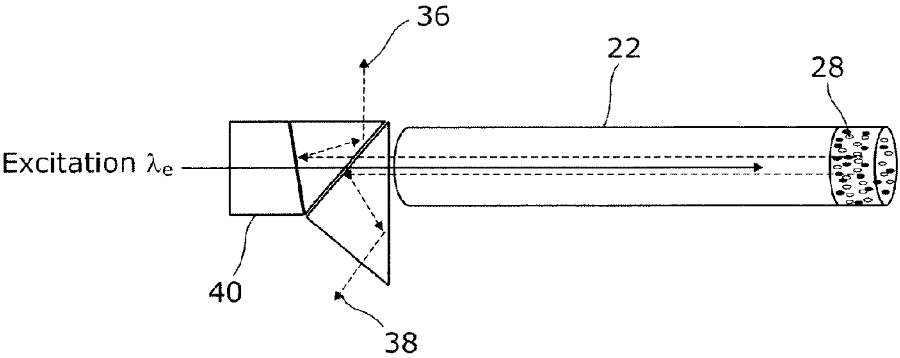

Excitation pulse
Amplitude (a.u)
Emission lifetime
Increasing O_2 concentration
Measurement window
Time (μs)

Figure 4


36
22
28
Excitation λ_e
40
38