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A Dissolved Oxygen Measurement Based on Fiber Optical Oxygen Sensor

[1,2] **Shaofei WU**
[1] Hubei Province Key Laboratory of Intelligent Robot, Wuhan Institute of Technology
[2] School of Computer Science and Engineering, Wuhan Institute of Technology, Wuhan, China
E-mail: wushaofei@wit.edu.cn

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Abstract: For the determination of dissolved oxygen, working principle of the fiber optic oxygen sensor is studied. The sensor system calibration method and temperature compensation measures and their maintenance methods are analyzed. The dissolved oxygen sensors current widely using oxygen electrode and optical fiber oxygen sensor are compared. Optical fiber probe sensor is used in the current system, the multiple points and multiple samples can achieve the simultaneous detection. *Copyright © 2013 IFSA.*

Keywords: Oxygen measurement, Fiber optic oxygen sensor, Quenching, Ruthenium compound.

1. Introduction

Dissolved oxygen (DO) refers to the molecular state oxygen dissolved in the water. It is vulnerable to physical factors (including water temperature, barometric pressure, salinity and so on) and biochemical factors (water body organic content, inorganic substance oxidation and so on) influence. The dissolved oxygen (DO) detection has extremely vital significance in aquaculture, medicine, environmental and industrial process and other fields. At present, the commonly used measurement methods mainly include iodometric titration, the oxygen electrode law and the luminescence analytic method and so on. Ramamoorthy [1] has made the exhaustive introduction to the above each method's principle and their application in the different environment. Compared with the current method, optical oxygen sensor is more attractive. In the sensing process, it does not consume the oxygen, does not need the reference electrode, does not disturb by the outside electromagnetic field. It has nothing to do with the sample's flow rate and the stirring rate. The response is fast, and it does not use the connection electric current. Therefore, in recent decades, the optical sensor's research is very active.

Optical sensors take the fluorescence (phosphorescence) as a means. It uses special union between the acceptor and the external species. It realizes to object’s qualitative and quantitative determination. To most fluorescence (phosphorescence) species, oxygen is universal and efficient quenchers. It achieves oxygen detection by detecting the sensing element’s optical signal changes (luminous intensity or luminous life, etc.). In general, by fixing the sensing element on the oxygen permeable polymer film, optical thin-film oxygen sensor was obtained [2]. The fixing method of fluorescence (phosphorescence) species is one of keys which optical thin-film oxygen sensor was successfully made. The fixing methods were divided into the following three: (1) physical embedding method; (2) covalent cross-linking method; (3) sol-gel method. In this paper, fiber-optic oxygen sensors, which used ruthenium compounds as a sensing element and using sol-gel method, is a coupling phase fluorescent sensor.

2. The Working Principle of Fiber Optic Oxygen

Oxygen molecule that is a kind of triplet molecule can effectively quench fluorescence and phosphorescence some other luminous body. This phenomenon is known as "dynamic fluorescence quenching" [3-4]. The so-called fluorescence quenching refers to the physical or chemical processes of leading to the fluorescence intensity decline between fluorescent substance and solute molecules or solvent molecules. The substance which fluorescent material molecules interaction causes the strength decline is known as fluorescence quenchers. Fluorescence quenching process is actually that the light competes with each other and thus emitting excited state shortens the lifetime process. In the excitation state, the oxygen molecules colliding with the fluorescent group lead to the non-radiation energy conversion. The degree of fluorescence quenching relates to collision frequency, and also relates to the media concentration of oxygen, pressure and temperature. Quenching generally divided into static quenching and dynamic quenching.

Static quenching: assuming the dissolved oxygen and luminescent molecules forms ground state complex, quenching equation can be expressed as:

$$\frac{I_0}{I} = 1 + kP_{o_2} \tag{1}$$

In this equation, k is the complex formation constant, I_0 and I are the luminous intensity when dissolved oxygen was not present and present.

The characteristic of Static quenching is that a light absorption spectrum may change. Temperature rise can lead to luminescence enhancement, and luminescence lifetime does not change.

The dynamic quenching mechanism is more complex, including the collisional quenching, energy transfer quenching, electron or charge transfer quenching, clustered systems quenching and so on.

In solution, the fluorescence quenching of oxygen molecules is more complex. Now fluorescence quenching mechanism that has confirmed through laser flash spectroscopy is: the excited singlet state fluorescent reagents molecules $^1M^*$ encountering with the oxygen molecules form compounds, and greatly enhances $S_1 \to T_1$ intersystem crossing process in $^1M^*$. The excited triplet state $^3M^*$ may not only be quenched by the collision with dissolved oxygen and other impurities, and can also occur to the following reaction leading to the triplet quenching:

$$^3M^* + ^3M^* \to ^1M^* + M \tag{2}$$

$$^3M^* + M \to ^3(M^*M) \to M + M + T \tag{3}$$

During the luminescence lifetime, the entire quenching process completed, and it shortened the light-emitting life. According to steady-state hypothesis, Stem-Volmer equation can be got:

$$\frac{I_0}{I} = 1 + K_{SV}\left[P_{o_2}\right] \text{ or }, \quad \frac{\tau_0}{\tau} = 1 + k_q\tau_0\left[P_{o_2}\right] \tag{4}$$

where $K_{SV} = k_q\tau_0$ is the Quenching constant of Stem-Volmer. Its characteristics are: temperature increasing led to quenching increase; luminescence lifetime reduced along with quencher concentration increasing.

Measured dissolved oxygen concentration can change the intensity of fluorescence radiation, and also change the life of fluorescent radiation. Therefore, the detection method was accordingly divided into two kinds. One is to measure the fluorescence radiant intensity, and the other is to measure the fluorescence radiant lifetime. From the Stem-Volmer equation can be seen that whether measured fluorescence intensity or measured fluorescence lifetime, the concentration information of the measurand can be got. The material's fluorescence intensity is vulnerable to external factors. Although the measurement of fluorescence lifetime measurement is more complex than the fluorescence intensity, the fluorescence lifetimes value of fluorescent substances is its own intrinsic parameters. Therefore, the fluorescence lifetime measurement was not affected by external factors change (such as light intensity, etc.), having good anti-jamming capability.

Ideally, assuming t = 0, the incentive disappears. General fluorescence lifetime is defined as follows:

$$\tau = \frac{\int_0^\infty t \cdot I_f dt}{\int_0^\infty I_f dt} \tag{5}$$

I_f is the fluorescence intensity signal which it is changed with time. In fact it is similar to a single exponential decay function, and it can be described in the following formula:

$$I_f = I_0 \cdot \exp(-t/\tau_c), \tag{6}$$

where τ_c is the exponential decay time constant.

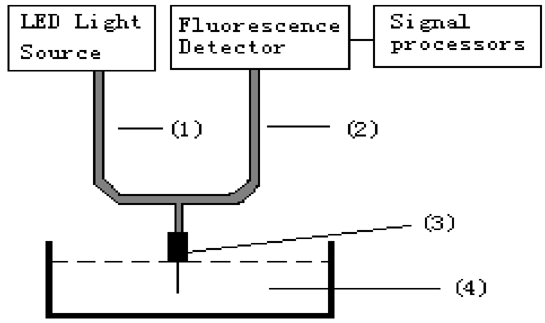
In this paper, optical fiber oxygen sensor uses sol-gel fixation method, and it uses the fluorescence of ruthenium compound to measure the oxygen partial pressure: The emission wavelength of pulsed blue LED is about 475 nm, and fiber-optical transmits light to the dissolved oxygen probe. The probe tip is composed of thin layer which is made in waterproof-sol-gel material. The sol-gel matrix can fix and protect the internal ruthenium compound. On the tip of the detector, LED light excited the ruthenium compound fluorescing. The emission energy wavelength is about 600 nm. If the excited ruthenium compound encounters an oxygen molecule, through non-radioactive conversion, the excessive energy of ruthenium compound transfer to molecular oxygen, reducing or quenching the fluorescence signal. The degree of quenching is related to oxygen concentration levels or thin-film the partial pressure of oxygen, and in the sample achieves oxygen dynamic balance. Detectors collect energy that was transmitted to the spectrometer through the optical fiber. A/D converter converts the analog data into the digital data, displaying on the spectrum analyzer.

3. Fiber Optic Oxygen Sensor System Components

In theory, optical fiber oxygen sensor detects oxygen partial pressure. When the temperature is kept constant, the weight of the liquid dissolved oxygen is proportional to the pressure of the gas on liquid surface. Therefore, the gas pressure on liquid surface is proportional to the concentration of the gas in the liquid. If the absolute pressure is known, the concentration (mol %) can be calculated: the mole fraction = oxygen partial pressure/absolute pressure. Optical fiber oxygen sensor can detect the partial pressure of oxygen, which in gas environment the reaction is similar to the reaction of gas balance in liquid environment. Therefore, in the gas environment this system can be adjusted, and then applying to liquid samples is feasible.

The fluorescent emitting from the ruthenium compound spreads in all directions. In the pure medium, only the fluorescence towards optical receiver angle of the detector can be detected. If the probe tip close to a reflective surface or immersed in a highly scattering medium, the fluorescence signal will be strengthened. This strengthening is proportional to the fluorescence intensity which it is in a certain oxygen pressure and under the zero-pressure. But it does not affect the Stern-Volmer coefficient. For this reason, the intensity of fluorescence must be measured under zero-pressure of oxygen.

The excitation light source in the dissolved oxygen measurement system used the modulated emitting diode LED. Bifurcation Optical fiber was transduction carrier of light signal. The sensor is fiber sensing probe having the fixed-sensitive membrane. The fluorescence signal by the photoelectric conversion was detected, processed and output. Fiber optic oxygen sensor system structure is shown in Fig. 1.



(1) Excitation optical fiber, (2) Receiving optical fiber, (3) Sensing material probe, (4) Sample cell.

Fig. 1. Fiber optic oxygen sensor system structure.

4. Optical Fiber Oxygen Sensor's Calibration and Temperature Compensation

For the sample's accurate measurements of dissolved oxygen, optical fiber oxygen sensor system firstly perform a calibration procedure. Here, the main consideration is whether the temperature changes of the sample compensate or not. If the sample is no temperature fluctuations or temperature fluctuations less, it does not require temperature compensation. In the following, taking the Linear (Stern-Volmer) rule as an example, how fiber optic oxygen sensor system calibrates is introduced.

Stern-Volmer algorithm requires at least two standards of known oxygen concentration. The first standard must be absolutely no oxygen concentration, the second standard must be the highest oxygen concentration in working range. Fluorescence intensity can be expressed by Stern-Volmer equation, and in the number fluorescence is associated with the partial pressure of oxygen.

On a specific medium, at constant total pressure and temperature, the partial pressure is proportional to the oxygen mole fraction. Stern-Volmer constant (k) firstly depends on the chemical composition of ruthenium compound. In the detector, Stern-Volmer constant (k) is related to the temperature. All measurements should be carried out under the same temperature, using same calibration tests and temperature monitoring equipment.

If the temperature wants to compensate, the relationship of Stern-Volmer value and temperature is defined as follows:

$$I_0 = a_0 + b_0 \times T + c_0 \times T^2 \tag{7}$$

$$k = a + b \times T + c \times T^2 \tag{8}$$

Under oxygen zero pressure, fluorescence intensity (I_0) depends on the system's optical configuration: power source, fiber, fiber-coupled detector and the light loss generating by fiber coupling, the sample's backscattering. When the configuration changes, fluorescence intensity (I_0) should be re-measured under oxygen zero pressure. Sensor is more sensitive to low oxygen concentration. The photometer's signal-to-noise ratio is approximately proportional to square root of the signal intensity. At low oxygen concentration, oxygen concentration changes will cause the signal strength's significant change.

Temperature affects the fluorescence intensity and the collisional frequency of the oxygen molecules with the fluorophore. Temperature also affects the solubility of oxygen in samples. The net effect can be seen as a change of the calibration slope. To ensure accurate measurement results, the sample detection must be carried out at a constant temperature. If the temperature cannot be guaranteed, when dissolved oxygen concentration measurement was carried out, the temperature measurement should be synchronously carried out to access to temperature data. Through the sensor system software, the readings of oxygen are automatically corrected according to the temperature data.

5. Maintenance of Fiber Optic Oxygen Sensor System

Ambient light will affect the detector. So the detectors should be installed in a sealed container to block ambient light, or in a dark room shielded detectors. And the detector uses a silicon rubber protective coating to eliminate the impact of ambient light. Protective coating slows down the whole system response time, the data shows that: slower 30-50 s in the liquid, and slower 20-30 s in the gases.

Glass is sensitive to high alkaline environment, and encountered HF (hydrogen fluoride) it will have a serious physical wear and tear. Glass has immunity to the common organic solvents. If the coating is damaged or destroyed, the detector can be re-sprayed. In the test with HF (hydrogen fluoride) solvent, the coating should be pay attention to protective. Measurement accuracy was also affected by the competing compound fluorescence quenching, for example: F2, Cl2 and Br2, However, their quenching efficiency has yet to be assessed.

6. Conclusion

Oxygen sensing probe is very easy to maintain. When it is not in use, it can place in the air for long-term, but it should not expose to the excitation light source. The dropping of probe will damage Optical fiber. Do not over tighten connectors. Cleaning the probe can use 10 % hypochlorite detergent, and use gamma rays or sodium hypochlorite to disinfect.

Comparing to dissolved oxygen measurement with the current large-scale use of oxygen electrode sensors, optical fiber oxygen sensor has the following characteristics: measures both oxygen gas and dissolved oxygen in gases and liquids; immune to environmental changes in pH, salinity and ionic strength; immune to interference from moisture, carbon dioxide, methane and other substances; fast response time; does not consume oxygen, allowing for continuous contact with the sample; frequent calibration is unnecessary; probe temperature range wide. Optical fiber probe sensor is used in the current system, the multiple points and multiple samples can achieve the simultaneous detection.

While fiber optic oxygen sensor has not been a large number of commercial applications, but based on its large number of advantages, we have reason to believe that the dissolved oxygen measurements in the near future obtained in the leading position. The current research focus include: first, looking to and developing more excellent sensing reagents and immobilized materials; secondly, developing portable phosphorescent oxygen sensor; third, the sensors immobilized; fourth, the sensor temperature compensation and maintenance.

Acknowledgements

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