Research on Key Technologies of On-line Oxygen Concentration Measuring Instrument

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Abstract. When applied in a coal mine, oxygen concentration monitoring will be affected by changes in temperature and pressure, which will cause large deviations in the measured values. In this paper, by integrating oxygen concentration monitoring, temperature monitoring, and pressure monitoring, by finding the functional relationship between the oxygen concentration monitoring value and the pressure value and temperature value at different pressures and temperatures, the effect of temperature and pressure changes on the measurement accuracy of oxygen concentration is eliminated. Based on the analysis of the influence of ambient temperature and pressure, a method of temperature and pressure compensation is proposed. It has been tested that the thermal stability time of the oxygen sensitive element is controlled within 30s, and within the range of (-10 ~ 50) °C and (50 ~ 120) kPa, the measurement error of the compensated oxygen concentration is less than 2.5% FS.

1. Introduction

Mine disaster is the most intractable emergency problem that mankind facing by far, which is also one of the most complex challenges in the mineral resource exploitation in 21st century. The amount of China’s natural coal exploration and production is always ranked first in the world. People have always been troubling by the serious illegal operation accidents and major casualty accidents in the mine, which are caused by a variety of geological disasters, illegal operations and other factors, especially the most serious drilling accidents in coal mines, which cause serious losses not only to the life and property of mine operators, but also to the state-owned assets, and also easily form a negative impression of coal mine insecurity in the society with extremely bad influence [1]. To ensure the safety of the underground operators’ working condition and their life and property, a working environment similar to the ground is necessary, which indicates that the oxygen concentration is an important indicator. When the oxygen concentration in the roadway air decreases, people will be difficult to breath, which will even lead to death due to lacking oxygen. The article 135 of current “Coal Mine Safety Regulations” stipulates that the oxygen concentration in the intake air flow of the mining face should be not less than 20% [2], which aims to ensure the safety of life and property of coal mine workers. In addition, the oxygen concentration is likely less than 18% in the excavation roadway with poor air feeding conditions, the roadway near the flammable coal seam, the subsidence area of goaf or the roadway defined as highly gassy and outburst-prone mine, which may affect the safety of the underground working personnel. Therefore, for real-time online monitoring and providing working instruction, a fully reliable monitoring instrument for the oxygen concentration on site is indispensable.

The sensors of the coal mine monitoring system include oxygen concentration monitoring instruments. The real-time online monitoring of the oxygen concentration in underground coal mines
and refuge chambers should adopt the monitoring measures of “On-site sampling, on-site handling, on-site monitoring, and on-site guiding”. However, the humidity, temperature, and pressure in the underground environment of the coal mine will change suddenly with the changes of working conditions, and the changes in humidity, temperature, and pressure have significant impact on the accuracy of the sensor measured value. Therefore, it is a key method that how to eliminate the influence of these factors on the measurement accuracy of the oxygen concentration detection instrument in coal mines.

2. Basic principle of oxygen detection

2.1. Principle of oxygen concentration detection with fluorescence quenching
Molecular oxygen (O2) is a well-known collision quencher, and its triplet molecule can effectively quench the fluorescence of any fluorophore. Because of the molecular oxygen characteristics of neutrally charged and small molecular size and the advantages that using molecular oxygen as a quencher has high collision efficiency and high diffusion coefficient, the quenching degree mainly depends on the environment O2 concentration. Based on this sensing mechanism, ruthenium complex is widely used. In the oxygen concentration measuring, the quenching reaction of the fluorophore is mainly caused by the collision and reaction between the triplet fluorophore (such as other molecules in the ground state complexing with ruthenium) and other quencher in the ground state (such as the triplet molecular oxygen), then the ruthenium complex returns to the ground state without emitting photons, and the oxygen molecular changes from the ground state to the excited state, thereby the oxygen concentration in the environment can be measured. The dynamic quenching process is shown in Figure 1.

Assuming that the quenching process of the fluorophore with molecular oxygen is simply due to collisions, the oxygen partial pressure ($\rho$O2) is related to the emission intensity and the lifetime of excited state, which can be described by the Stern-Volmer equation:

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + \kappa_q \cdot \rho_O \cdot \tau_0 = 1 + K_D \cdot \rho_O$$

(1)

In the equation, $\rho_O$ is the partial pressure of O2, $I_0$ and $\tau_0$ are the fluorescent intensity and the fall time of the fluorophore without oxygen, $I$ and $\tau$ are the fluorescent intensity and the fall time of the fluorophore with a certain concentration of oxygen, and $K_D$ is a dynamic constant.

According to Dalton’s law, for an ideal mixed gas with any specific volume, if there is no chemical reaction between these gas components, the total pressure ($P_{total}$) generated by them will be equal to the sum of gas partial pressure ($P_i$) of each component gas.

$$P_{total} = \sum_{i=1}^{k} P_i$$

(2)

From Equation (2), we can infer that the ratio of the molecules number ($N_i$) of each component gas to the total molecules number ($N_{total}$) of the ideal mixed gas can be approximately equal to the ratio of
the partial pressure \( (P_i) \) of each component gas to the total pressure \( (P_{total}) \) of the ideal gas mixture.

\[
\frac{N_i}{N_{total}} = \frac{P_i}{P_{total}}
\]

From the calculation formula of using fluorescence quenching to detect oxygen concentration, we can know that, in a certain ideal space environment, the concentration of oxygen is directly related to the partial pressure of the oxygen and the total atmospheric pressure, that is, it is proportional to the partial pressure of oxygen, and inversely proportional to the total atmospheric pressure. In addition, the principle of detecting oxygen concentration with fluorescence quenching is also one of the basic principles of optical detection technology, which has the characteristics of lossless and strong anti-interference. It means that this method has higher detection accuracy, stronger interference resistance ability and better long-term stability than the electrochemical oxygen detection technology, which is also in line with the development and research direction of mine oxygen concentration sensors to improve the reliability and accuracy of oxygen concentration detection in recent years. The traditional fluorescence quenching oxygen sensor is composed of a closed gas chamber, a luminous diode, an internal optical path lens, a photodetector, and a matching demodulation circuit, as shown in Figure 2.

![Figure 2. Schematic diagram of traditional fluorescence quenching oxygen sensor](image)

2.2. Research and test of sensor’s anti-humidity technology

Under the high-temperature and high-pressure environment, water will be condensed on the optical path lens surface inside the sensitive element, which will change the fluorescence lifetime and cause measurement failure. In order to avoid the influence of humidity on the measurement, the adaptive anti-condensation technology was studied.

The adaptive anti-condensation technology for sensitive elements requires a design method that combines structure, software and hardware. First, for the preparation of the anti-condensation structure, the cermet heating element and the metal powder were first prepared into a ring structure by mechanical interference fitted, and then the sensitive element was embedded in the structure to encapsulate as a whole; then, for the adaptive adjustment of anti-condensation, a humidity measurement device and a metal ceramic heating element collection control device were added to collect real-time humidity data, control the intelligent closed-loop of the metal ceramic heating element, and maintain the working environment humidity of sensitive element in the structure satisfying reliability requirement of \( RH<90\% \). The sensitive element structure is shown in Figure 3.

![Figure 3. Sensitive element structure composition diagram](image)
In order to verify the actual effect of the adaptive anti-condensation technology of sensitive elements, a comparative test was conducted in a simulated humidity generating device, and two test schemes were adopted: Scheme 1: the sensor was placed in an environment with a humidity of RH <50%, and after running for 20 minutes, the environment humidity around the device was increased to larger than 95% RH and the data was record in 10 minutes; Scheme 2: the sensor was placed in an environment with the humidity RH> 95% for 100 minutes, running for 10 minutes, and the data was recorded. The test data is shown in Figure 4, and the test results show that this sensor can effectively control the measurement error for 30s in an environment with humidity RH> 95%, and the error caused by humidity is controlled within 2.0% FS.

![Figure 4. Sensor humidity error test (20.9%)](image)

3. Temperature compensation technology and testing

3.1. Effect of temperature on oxygen concentration measurement

According to the Stern-Volmer equation, the lifetime of the excited state depends on the decay rates of radiation ($k_r$) and non-radiation ($k_{nr}$). $K_D$ and $\tau_0$ is related to the quenching constant. Therefore, the dynamic quenching mechanism is a process related to diffusion, which is extremely susceptible to temperature sudden changes. The higher the temperature, the faster the diffusion rate, which causes a large amount of collision quenching, and then affects the measurement concentration and leads to reading error. Therefore, it is very important to correct the temperature by “mapping” the SVP on multiple temperatures. Taking the oxygen concentration at 20% as an example, as the experimental data shown in Figure 5, the change rate of the concentration value within a temperature range of -10°C to 50°C is 16%.

![Figure 5. Effect of temperature on oxygen concentration measurement](image)

In addition, the signal amplitude of the sensor is also affected by the working band of the fluorescent source, the internal optical path lens and the calculation algorithm of the sensing element etc., and the mathematical relationship of temperature influence cannot be calculated by the determined functional relationship. Therefore, in this paper, we firstly obtain the law of oxygen concentration data under temperature changing through simulated temperature test, and then compensate for temperature using empirical mathematical formula.
3.2. Temperature compensation method

The temperature compensation includes two stages. The first stage is to obtain the functional relationship of the influence of temperature on oxygen concentration: First, in the temperature compensation range of -10℃~50℃, the differences between the measured values of the sensor and the true values of standard oxygen concentration at different O2 concentrations of 0% O2, 5% O2, 10% O2, 15% O2, 20% O2, 25% O2 were obtained. The experiment used a high-precision, high-efficiency, high and low temperature test chamber for the temperature compensation stage test. Each oxygen concentration measurement point was selected at every 5°C within the temperature compensation range of -10℃~50℃. Each oxygen concentration test point selected a total of 6 oxygen concentration test points of 0% O2, 5% O2, 10% O2, 15% O2, 20% O2, 25% O2. During the temperature test, the standard sample gas was introduced to each sensor and the display value of the oxygen concentration sensor without temperature compensation was recorded at the same time. The temperature test data results are shown in Figure 6.

![Figure 6. Influence of temperature on the measurement of oxygen sensor](image)

First, under the conditions of constant oxygen concentration and different temperatures, the piecewise linear calculation and measurement error fitting to the measurement errors were carried out using the least square method, and the straight line slopes of $K_{-10}$, $K_{-5}$, $K_0$, ..., $K_{50}$ between each adjacent test point were calculated.

$$C'(T) = k_i C'(T) + C'(T), \quad T_i \leq T \leq T_{i+1}$$ (4)

Secondly, under the condition of constant temperature and different oxygen concentrations, the piecewise linear calculation and measurement error fitting to the measurement errors were carried out using the least square method, and the straight line slopes of $k_0$, $k_5$, ..., $k_{50}$ between each adjacent test point were calculated.

$$C''(T) = k'_i C''(T) + C''(T), \quad C_i \leq C \leq C_{i+1}$$ (5)

Finally, the cyclic compensation and judgment are carried out by substituting data into the temperature function relationships (4) and (5): In the first step, the sensor obtains the oxygen concentration value $C'$ of the measurement environment (without cyclic compensation) and the temperature value $T$ of the corresponding environment; In the second step, the corresponding oxygen concentration value $C'$ measured on site (without cyclic compensation) and the temperature value $T$ of the corresponding environment are substituted into the empirical compensation formula (4) to obtain the oxygen concentration value $C''$ with the first empirical compensation. In the third step, the oxygen concentration value $C''$ after compensation in the second step and the temperature value $T$ of the corresponding environment are substituted into the empirical compensation formula (5) to obtain the oxygen concentration value $C''$ with the second empirical compensation. Finally, after each round of the second and third steps of the empirical compensation process, it is judged whether the oxygen concentration value after the cyclic compensation satisfies the accuracy judgment condition $|C_i - C_{i+1}| \leq 0.01$, and the cyclic compensation will stop when the judgment condition is satisfied.
3.3. Test
The O2 standard gas with a concentration of 20% was introduced into the sensor, and the accuracy tests before and after the compensation were carried out in the temperature range of -10°C ~ 50°C, and the relative error of the oxygen concentration was calculated, as shown in Table 1.

| Temperature/℃ | Uncompensated | After compensation | Relative error | After compensation | Relative error |
|---------------|---------------|--------------------|----------------|--------------------|----------------|
| -10           | 18.4          | 19.8               | -8.0%          | 19.8               | -1.0%          |
| 0             | 18.9          | 19.8               | -5.5%          | 19.8               | -1.0%          |
| 10            | 19.4          | 19.9               | -3.0%          | 20.0               | 0.0%           |
| 20            | 19.9          | 20.0               | -0.5%          | 20.0               | 0.0%           |
| 30            | 20.5          | 20.0               | 2.5%           | 20.0               | 0.0%           |
| 40            | 21.1          | 19.9               | 5.5%           | 19.9               | -0.5%          |
| 50            | 21.5          | 21.5               | 7.5%           | 21.5               | -0.5%          |

4. Pressure compensation technology and test

4.1. Influence of pressure on the oxygen concentration measurement
As can be seen from Dalton's law, in an ideal state, the partial pressure ratio of a mixed gas exhibits an ideal ratio. However, when the pressure changes, the intermolecular force will increase or decrease, thereby changing the partial pressure of each component gas. The change of the total atmospheric pressure will affect the proportion of oxygen concentration, thereby affecting the accuracy of oxygen concentration measurement. Taking a gas with an oxygen concentration of 20% as an example for data simulation, the change rate of the oxygen concentration is shown in Table 2.

| Pressure(KP a) | Standard concentration value | Measurement Value | Error %O2 | relatively Rate of change /% |
|----------------|-----------------------------|-------------------|-----------|-------------------------------|
| 120            | 20.0                        | 19.0              | -1.0      | -5                            |
| 110            | 20.0                        | 19.5              | -0.5      | -2.5                          |
| 100            | 20.0                        | 20.0              | 0.0       | 0 (Benchmark)                 |
| 90             | 20.0                        | 20.6              | 0.6       | 3                             |
| 80             | 20.0                        | 21.0              | 1.0       | 5                             |
| 70             | 20.0                        | 21.6              | 1.6       | 8                             |
| 60             | 20.0                        | 22.0              | 2.0       | 10                            |
| 50             | 20.0                        | 22.5              | 2.5       | 12.5                          |

It can be seen from the above data that as the total atmospheric pressure decreases, the proportion of oxygen concentration gradually increases; as the total atmospheric pressure increases, the proportion of oxygen concentration gradually decreases. Therefore, in the process of the monotonous increase of total atmospheric pressure, the oxygen concentration shows a monotonous downward trend.

4.2. Pressure compensation method
The core design idea of the pressure compensation algorithm is using the oxygen concentration data and atmospheric pressure measurement data measured by the preliminary experiments, adopting the cyclic compensation method, and combining the piecewise linear interpolation method and the gravity center Lagrange interpolation method to gradually approximate the actual oxygen concentration, complete pressure compensation of oxygen concentration value. The pressure compensation algorithm includes
the following stages:

(1) In the range of 50 kPa ~ 120 kPa atmospheric pressure, air pressure test points of \( P_1, P_2, P_3, \ldots, P_n \) were uniformly selected, the oxygen concentration test points of \( C_1, C_2, C_3, \ldots, C_n \) were selected in the O2 measure range of 0% ~ 25%, and the standard atmospheric pressure and ambient oxygen concentration were determined as the original pressure \( P_0 \) and oxygen concentration reference point \( C_0 \), the empirical function \( A_{cb}(P_a) \) of oxygen concentration-atmospheric pressure influence was measured and calculated.

(2) After changing the atmospheric pressure environment, the oxygen concentration value \( C' \) and atmospheric pressure value \( P' \) obtained by the sensor were substituted into the oxygen concentration-atmospheric pressure influence function \( A_{cb}(P_a) \) to calculate the corresponding slope \( F(C',P') \).

(3) The slope \( F(C',P') \) was used to compensate the influence of the atmospheric pressure change value on the oxygen concentration value, and the oxygen concentration value \( C'' \) after each compensation was calculated.

(4) The calculated value \( C'' \) was substituted into (2) ~ (3) again to perform the cyclic compensation calculation. When the absolute value of the difference between the oxygen concentration values after the two cyclic compensations is less than the preset judgment value, the cyclic compensation was stopped, and the oxygen concentration value after the last cyclic compensation was taken as the oxygen concentration measurement value \( C_2 \).

4.3. Test

The comparison experiment of pressure compensation was performed using an oxygen standard gas sample with a concentration of 20.0% O2. In the pressure range of 50 kPa ~ 120 kPa, and the measured value of oxygen concentration without pressure compensation has a fluctuation range of -5.0% ~ 12.5%; After the pressure compensation, the measured value fluctuation range of the oxygen concentration significantly reduced to -1% ~ 2.0%, indicating that after pressure compensation the influence of the pressure change on the measured value of the oxygen concentration has been reduced to the range of 2.5% FS, and the results are shown in Figure 7. The comparison test results show that, after the oxygen sensor has been compensated for atmospheric pressure, the effect of the atmospheric pressure change in the coal mine tunnel on the measured value of oxygen concentration is basically eliminated, and the error is less than 2% FS.

![Figure 7. Changes of sensor measurement value with pressure before and after pressure compensation](image-url)

5. Conclusion

Through introducing the importance of oxygen concentration measurement in coal mines, this paper proposes an on-line sensor for oxygen concentration measurement with strong adaptability. Firstly, by using the element structure and adaptive anti-condensation technology, the effect of water condensing on the lens surface of the element optical path on the measurement data of oxygen concentration is eliminated. Then the influence curves of temperature and pressure changes on the oxygen concentration measured value were obtained using the simulation experiment method. The functions about the
influence of temperature and atmospheric pressure on the oxygen concentration measurement were carried out, and the corresponding temperature compensation algorithm and pressure compensation algorithm were obtained. Finally, in the laboratory simulation test, the above compensation algorithms were tested and verified. The test data shows that this sensor can adapt to the high-precision measurement of oxygen concentration in the temperature range of -10℃ ~ 50 ℃ and pressure range of 50 kPa ~ 120 kPa, and after compensation, the measurement error is less than 2.5% FS.

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References
[1] Gu Xiaobo, Tang Mingjun, Ye Junming. Causes and Countermeasures of Coal Mine Safety Accidents [J]. Science and Technology and Enterprises, 2012 (5): 14.
[2] Xu Peng. Analysis of mine ventilation safety accidents and countermeasures [J]. Shandong Industrial Technology. 2018 (06): 55-57.
[3] Zhang Xuedian, Wang Yesheng, Wu Lei. Research on temperature compensation based on non-dispersive infrared CO2 concentration measurement [J]. Laser and Infrared, 2015, 45 (4): 412-415.
[4] Li Zhongyou. Structural principle and detection of oxygen sensor [J]. Practical Automobile Technology, 2008, 3: 31-32.
[5] Li Xuesheng, Lu Xinchun, Luo Xiaobing. Development of Dissolved Oxygen Sensor by Fluorescence Quenching Method [J]. Automation and Instrumentation, 2013, 04 (00): 17-20.
[6] Zhang Guangjun, Lv Junfeng. Research on compensation method of environmental impact in infrared gas analysis [J]. Journal of Beijing University of Aeronautics and Astronautics, 1996, 22 (6): 655-659.
[7] Zhou Dongqiu, Xiao Shaorong, Xiao Lin. Development of optical fiber dissolved oxygen sensor based on the principle of fluorescence quenching [J]. Optics and Optoelectronics Technology, 2013, 8: 64-66.
[8] Sipocz N, Tobiesen F A, Assadi M. The use of artificial neural network models for CO2 capture plants[J]. AppliedEnergy,2011,88(7):2368-2376.
[9] Zhang Haiqing, Liu Yan, Wang Hongjian. Research on the pressure compensation method of electrochemical gas measurement [J]. Coal Mine Electromechanics, 2014 (1): 30-32.
[10] Yang Jianhua, Hou Hong. Optical oxygen sensor based on the principle of fluorescence destruction [J]. Sensor Technology, 2001, 9 (20): 21-24.
[11] Yang Yirui. Research and design of dissolved oxygen concentration sensor based on the principle of fluorescence quenching [D]. Qingdao Technological University, 2017: 45-47.
[12] Jia Chuanwu. Research on phase demodulation method and stability and repeatability in fiber-optic oxygen sensor based on fluorescence quenching [D]. Shandong University, 2016: 11-15.
[13] Wang Hongjian, Tang Maofeng, Wang Xueling, etc. Design of high-precision mine oxygen sensor with temperature compensation [J]. Industrial and Mine Automation, 2012, 5: 63-65.
[14] Liu Yan, Zhang Libin, Jiang Ze. Design of mine infrared methane sensor with temperature and pressure compensation [J]. Industrial and Mine Automation, 2012 (8): 7-10.
[15] Chang Yu. Improved design of mine oxygen concentration sensor [J]. Coal Mine Machinery, 2018, 6: 105-107.
[16] Wang Lu. Development of a high-precision mine oxygen sensor with temperature and pressure compensation [J]. Energy Technology and Management, 2019, 6: 1-3.