

# Development of Carbon Monoxide Sensor Based on Composite Electrochemical Elements

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A carbon monoxide sensor with composite detection capabilities for carbon monoxide, hydrogen sulfide, and nitric oxide gases was developed using gas concentration detection technology based on composite electrochemical components to address the issue of cross-interference between exhaust gas and sulfur-containing gases from diesel vehicles and gas detection by mining carbon monoxide sensors. The sensor gas detection module includes two parts: a carbon monoxide hydrogen sulfide dual gas detection module and a nitric oxide gas detection module. The module is composed of gas detection components and signal detection circuits. An experiment was conducted to study the effects of hydrogen sulfide and nitric oxide gases on the detection results of carbon monoxide gas concentration. Through data analysis and linear fitting, a gas cross-interference compensation algorithm formula was obtained. The compensated carbon monoxide sensor experiment results show that the carbon monoxide sensor based on composite electrochemical elements has a measurement error of less than 5% in the mixed gas environment, meets the requirements of the AQ6205-2006 coal mine electrochemical carbon monoxide transducer, and can meet the technical requirements for the accurate detection of carbon monoxide gas of an underground rubber-tire truck transportation roadway.

## 1. Introduction

On October 12, 2021, the National Mine Safety Supervision Bureau issued the “Detailed Rules for Coal Mine Fire Prevention and Control”, establishing the principles of “prevention first, early warning, adaptation to local conditions, and comprehensive management”, which were implemented from January 1, 2022. These detailed rules propose to strengthen monitoring, precise analysis, and early warning.<sup>(1,2)</sup> By comprehensively utilizing the coal mine natural fire monitoring system, safety monitoring system, and manual inspection results, early warning is achieved on the basis of the “early warning value of coal seam oxidation carbon monoxide or goaf temperature to determine fire precursors”, providing a basis for optimizing and improving

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fire prevention measures, and achieving an early detection and disposal of underground fires.

As the main instrument for monitoring the concentration of carbon monoxide gas in coal mines, carbon monoxide sensors have played an important role in early fire warning and are currently the most mature and widely used fire warning and monitoring technology.<sup>(3–5)</sup> With the development of intelligent mining, precise detection has become an inevitable requirement for intelligent sensors. With the construction of high-yield and efficient mines, the number of underground rubber-wheeled vehicles is increasing. The exhaust emissions of such vehicles contain substances such as hydrocarbons, nitrogen oxides, sulfur dioxide, carbon monoxide, and smoke particles (certain heavy metal compounds, lead compounds, black smoke, and oil mist).<sup>(6–8)</sup> Among them, nitrogen oxides have a cross-interference effect on electrochemical carbon monoxide sensors, leading to frequent false alarm accidents of carbon monoxide sensors, seriously interfering with normal production in coal mines. Therefore, there is an urgent need to develop a carbon monoxide sensor with good gas selectivity that is not affected by the exhaust emissions of rubber-tire vehicles.

Many domestic and foreign researchers have conducted beneficial investigations by using laser spectral absorption technology with good gas selectivity to detect the concentration of carbon monoxide gas.<sup>(9)</sup> Jiang *et al.* proposed the development of a carbon monoxide sensor based on the tunable laser absorption spectroscopy technology TDLAS, using a 2330 nm laser, a small gas chamber, and a phase-locked module in the corresponding band. However, the sensor has a large volume and high cost, which is not conducive to its promotion and application.<sup>(10)</sup> Li *et al.* developed a mid-infrared differential CO detector using a pulse infrared thermal light source and a single detector dual-pass structure, but the instrument resolution was only 20 ppm, which does not meet the requirements of the coal mining industry standards.<sup>(11)</sup> Yin *et al.* proposed a dual resonant cavity differential structure photoacoustic cell to suppress the large background noise caused by high-power laser sources. A distributed feedback laser with a wavelength of 1566 nm was used as the excitation light source, and a fiber amplifier was used to pump the optical power to the 10 W level to detect CO gas. However, the sensor's power consumption was very high, which did not satisfy the requirements of intrinsic safety parameters for mining.

Electrochemical carbon monoxide sensors have the technical characteristics of high detection accuracy, low power consumption, and good stability.<sup>(12,13)</sup> Currently, they are the most mature and stable technology for detecting carbon monoxide gas. We adopt a carbon monoxide gas concentration detection technology based on composite electrochemical components to achieve the composite detection of carbon monoxide, hydrogen sulfide, and nitric oxide gas. Then, through cross-interference compensation methods, the problem of underground rubber-tire vehicle exhaust gas is solved. The issue of the impact of sulfur-containing gases on the accuracy of carbon monoxide gas detection, as well as the effective temperature compensation and correction of sensor concentration signals, is addressed by implementing hardware circuits and software algorithms.

## 2. Overall Design and Working Principle of Sensors

The electrochemical carbon monoxide sensing element consists of three catalytic electrodes, that is, a working electrode, a counter electrode, and a reference electrode, as well as a liquid electrolyte. When carbon monoxide and oxygen diffuse into the liquid electrolyte, an electrochemical oxidation or reduction reaction occurs.<sup>(14)</sup> The liquid electrolyte conducts electron transfer and outputs a current signal. The sensor circuit measures the magnitude of the current signal, which is used to calculate the concentration of carbon monoxide gas. However, the electrolyte containing carbon-monoxide-sensitive components can also undergo an electrochemical oxidation or reduction reaction in the presence of hydrogen sulfide and nitric oxide gases.<sup>(15)</sup> Therefore, when there is hydrogen sulfide or car exhaust containing nitric oxide in the environment, the sensitive components of the carbon monoxide sensor will also react, incorrectly indicating the concentration of the gas, leading to false alarms.

A carbon monoxide sensor based on composite electrochemical components is used to achieve the composite detection of carbon monoxide, hydrogen sulfide, and nitric oxide gas concentrations through the use of multiple sensitive elements such as carbon monoxide, hydrogen sulfide, and nitric oxide. Combined with a gas anti-cross-interference algorithm, the precise detection of the carbon monoxide gas concentration is achieved. The sensor principle is shown schematically in Fig. 1.

The sensor circuit mainly consists of a microprocessor, voltage conversion circuit, communication circuit, display circuit, sound and light alarm circuit, remote control receiving circuit, and gas detection module. The gas detection module includes two parts: a carbon monoxide hydrogen sulfide dual gas detection module and a nitric oxide gas detection module.

The sensor measures the initial concentrations of carbon monoxide, hydrogen sulfide, and nitrogen oxide gases by means of the gas detection module. As the carbon monoxide sensing

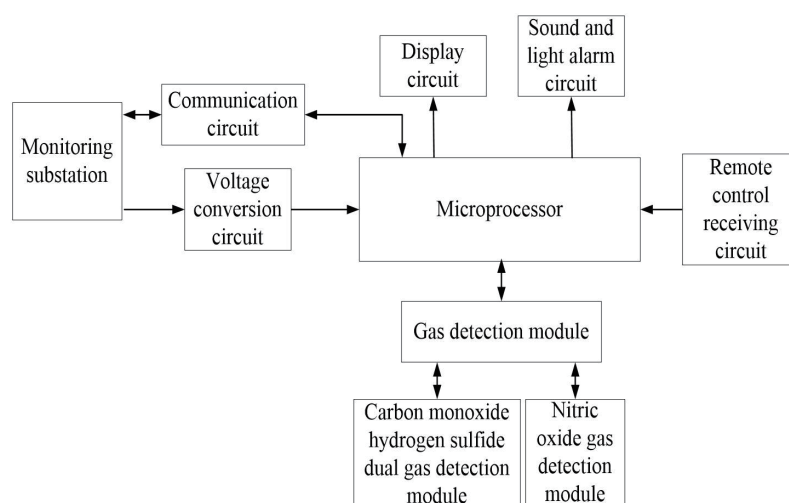


Fig. 1. Schematic circuit diagram of carbon monoxide sensor based on composite electrochemical components.

element has specific detection sensitivity to hydrogen sulfide and nitric oxide gases, the calculation for the actual concentration of carbon monoxide gas is introduced as

$$A_1 = A_0 - \alpha \times C_0 - \gamma \times B_0. \quad (1)$$

In the equation,  $\alpha$  and  $\gamma$  are cross-interference coefficients, which are determined through experimental methods to obtain a mathematical expression for accurately measuring the concentration of carbon monoxide gas in an environment containing hydrogen sulfide and nitric oxide gases; then, program programming can be accomplished.

### 3. Design of Gas Detection Module

According to Eq. (1), only the concentrations of carbon monoxide, hydrogen sulfide, and nitric oxide gases should be measured. Then, Eq. (1) is used to obtain the actual concentration of carbon monoxide gas in the environment. Therefore, the gas detection module, which includes a carbon monoxide hydrogen sulfide dual gas detection module and a nitric oxide gas detection module, is designed to convert the concentrations of carbon monoxide, hydrogen sulfide, and nitrogen oxide gases in the environment into electrical signals for measurement.

#### 3.1 Design of carbon monoxide hydrogen sulfide dual gas detection module

The carbon monoxide hydrogen sulfide dual gas detection module is composed of an electrochemical carbon monoxide hydrogen sulfide dual gas integrated gas detection component and a signal detection circuit. The gas detection element model is GS+4DT, with measurement ranges of 0–1000 ppm for carbon monoxide gas and 0–200 ppm for hydrogen sulfide gas. The resolution is 1 ppm and the response time is less than 30 s. The gas detection element adopts a four-electrode structure design with a carbon monoxide working electrode (CO Working), a hydrogen sulfide working electrode (H2S Working), and Counter and Reference electrodes. The electrode structure design is shown in Fig. 2.

When there is carbon monoxide or hydrogen sulfide gas in the environment, the electrolyte

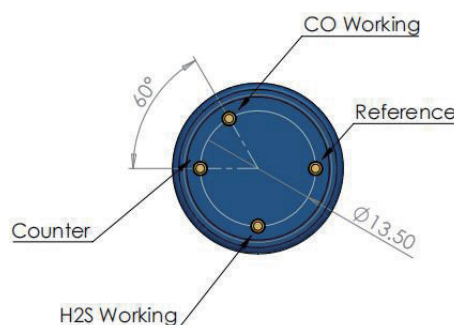


Fig. 2. (Color online) Electrode structure design of carbon monoxide/hydrogen sulfide dual gas integrated gas detection element.

inside the carbon monoxide/hydrogen sulfide dual gas integrated gas detection element undergoes the oxidation–reduction reaction. The carbon monoxide and hydrogen sulfide working electrodes will output corresponding weak current signals that are linearly related to gas concentration. The detection sensitivity of the carbon monoxide signal is  $80 \pm 30$  nA/ppm and that of the hydrogen sulfide signal is  $775 \pm 275$  nA/ppm.

The GS+4DT component is a zero-bias component, so the detection circuit of the carbon monoxide hydrogen sulfide dual gas detection module is composed of a constant-potential control circuit, a conduction circuit, and a current signal amplification circuit. The constant-potential control circuit is shown in Fig. 3.

The constant-potential control circuit consists of an operational amplifier U1, resistors R4, R5, and R6, and a capacitor C5. Its main function is to maintain the voltage between the reference electrode (Reference) and the working electrode (CO\_W) to control the electrochemical reaction and output a current signal corresponding to the target gas concentration. According to the virtual short-circuit characteristic of the operational amplifier chip, the voltages at pins 5 and 6 of the U1 operational amplifier chip are the same, always 1.2 VDC. According to the virtual break-circuit characteristic of the U1 operational amplifier chip, the current at pin 6 can be ignored, so there is no current passing through resistors R6 and R5, resulting in a voltage drop of 0 VDC. Therefore, the reference voltage of the GS+4DT component is always 1.2 VDC, while the internal resistance of the GS+4DT component is  $0 \Omega$ . Therefore, the voltage of the working electrode (CO\_W) is always 1.2 VDC, and this circuit is called a constant-potential control circuit. The GS+4DT component undergoes an oxidation or reduction reaction with the target gas, generating a current proportional to the gas concentration. This current must flow into the counter electrode through a constant-potential control circuit.

Figure 4 shows the conduction circuit after power failure, which is mainly used to eliminate the preheating balance time of the electrochemical components and ensure that the GS+4DT components can work normally after being powered on. Q1 and Q2 are depletion-type junction field-effect transistor devices with a P-channel and have the characteristic of a normally closed circuit after power failure. When the carbon monoxide hydrogen sulfide dual gas detection module circuit is disconnected from the power supply and in a nonpowered state, the drain and source electrodes of Q1 and Q2 are in a short-circuit conductive state with an internal resistance of less than  $300 \Omega$ . The working electrodes (H2S2 W, CO\_W) and reference electrodes (Reference) of the GS+4DT component are short-circuited together, so that the working electrodes maintain the same potential as the reference electrode. The internal electrochemical

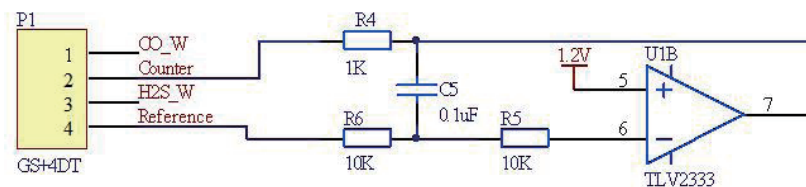


Fig. 3. (Color online) Constant-potential control circuit diagram.

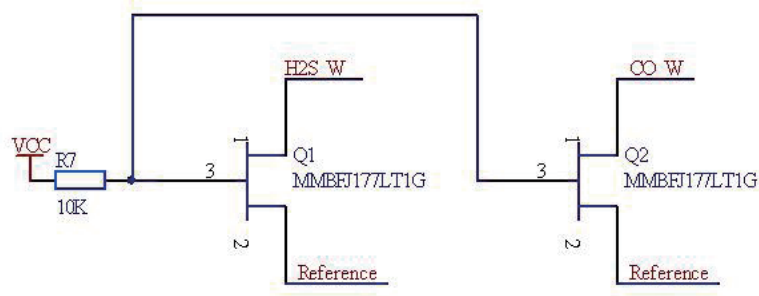


Fig. 4. (Color online) Circuit diagram of power loss and conduction.

reaction of the GS+4DT component remains stable, and the component can work reliably immediately after being powered on. When the circuit is powered on, the voltage between the gate sources of Q1 and Q2 is greater than the threshold voltage of 2.0 VDC, and the JFET device is in an open-circuit high-impedance state, which does not affect the normal working state of the working and reference electrodes.

Figure 5 shows the current signal amplification circuit diagram, consisting of operational amplifier chips U1 and U2, resistors, and capacitors. The signal current of the carbon monoxide working electrode (CO\_W) of the GS+4DT element passes through resistor R8, generating a signal voltage CO\_Vout proportional to the signal current of the carbon monoxide gas concentration. The signal current of the hydrogen sulfide working electrode (H2S\_W) passes through resistor R1, generating a signal voltage H2S2\_Vout proportional to the signal current of the hydrogen sulfide gas concentration, enters the A/D acquisition channel of the microcontroller to sample and calculate the signal current, and finally obtains the concentrations of carbon monoxide and hydrogen sulfide gases in the environment.

The design of the carbon monoxide hydrogen sulfide dual gas detection module has detection ranges of 0–1000 ppm for carbon monoxide and 0–200 ppm for hydrogen sulfide. The maximum range of the corresponding voltage signal is 1.2–3.0 VDC. Therefore, the resistances of the signal amplification resistors R1 and R8 in the current signal amplification circuit are calculated to be 10 and 20 k $\Omega$ , respectively.

### 3.2 Design of nitric oxide detection module

The nitric oxide detection module is composed of a nitric oxide component and a detection circuit. The nitric oxide component is also composed of a working electrode, a counter electrode, and a reference electrode. However, unlike carbon monoxide and hydrogen sulfide with zero bias voltage, the nitric oxide component requires a bias voltage of 300 mV for electrochemical reactions, so the detection circuit is also different from the dual gas component circuit. The circuit of the nitric oxide detection module is shown in Fig. 6.

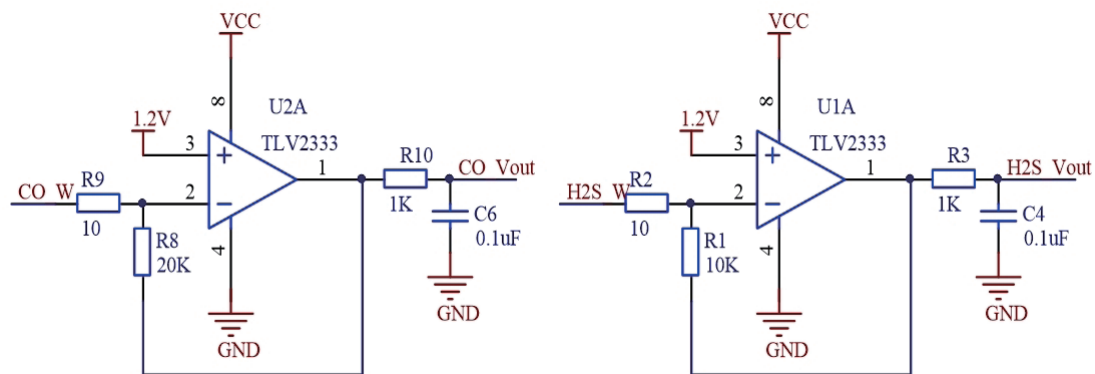


Fig. 5. (Color online) Current signal amplification circuit diagram.

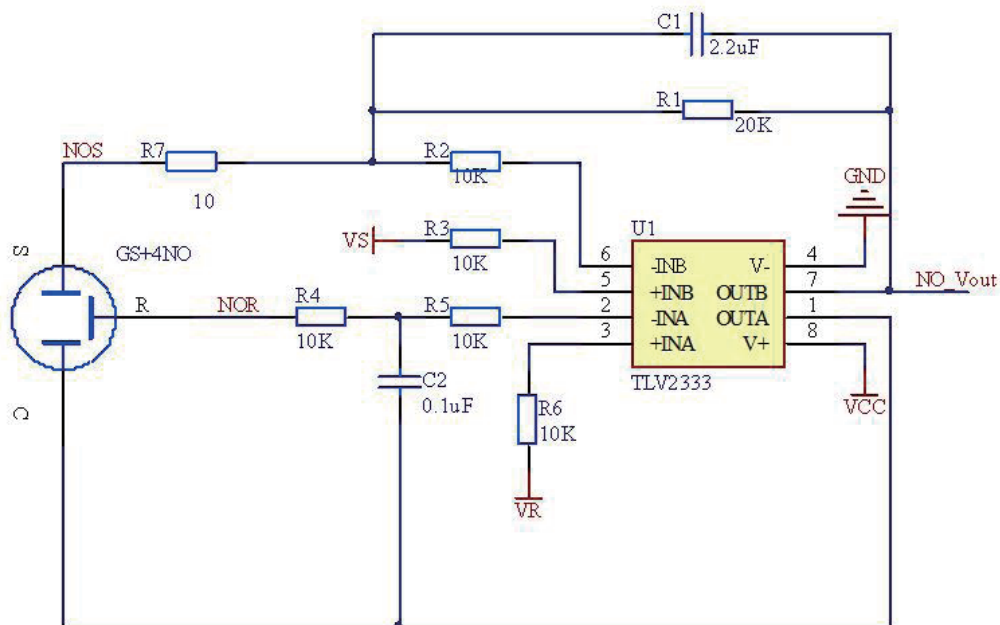


Fig. 6. (Color online) Nitric oxide detection module circuit.

The nitric oxide element model is GS+4NO, with a measurement range of 0–200 ppm. The detection circuit consists of an operational amplifier, a resistor, and a capacitor. To ensure a voltage difference of at least 300 mV between the working electrode (S) and reference electrode (C) of the GS+4NO component, a detection circuit is designed with a VS potential of 1.0 VDC and a VR potential of 0.7 VDC. On the basis of the virtual short- and virtual break-circuit characteristics of the operational amplifier chip, the voltage between resistors R7 and R2 is equal to the VS voltage, which is equal to 1.0 VDC. The detection sensitivity of the nitric oxide element is  $400 \pm 50$  nA/ppm. When the concentration of nitric oxide in the air is 0 ppm, the signal current is 0 nA, the voltage at both ends of resistor R1 is 0 VDC, and the voltage at NO\_



Vout is 1.0 VDC. When the concentration of nitric oxide is 200 ppm of the maximum range, the signal current is 80  $\mu$ A ( $400 \text{ nA/ppm} \times 200 \text{ ppm}$ ). To achieve a higher measurement resolution for the sensor, the A/D acquisition range of the microcontroller is 1.0–3.0 VDC, so the resistance of the current signal amplification resistor R1 is 20 k $\Omega$ . When the maximum range signal current is 80  $\mu$ A, the voltage at both ends of R1 is 1.6 VDC and the voltage at NO\_Vout is 2.6 VDC. Therefore, the voltage change at NO\_Vout corresponding to the measurement range of nitric oxide gas from 0 to 200 ppm is 0 to 1600 mV. The microcontroller can calculate the concentration of nitric oxide gas in the environment using the voltage amplitude at NO\_Vout.

#### 4. Gas Cross-interference Algorithm

The formula for calculating the concentration of carbon monoxide given in Eq. (1) is based on the redox reaction characteristics of the electrolyte of the electrochemical carbon monoxide element. Therefore, it is necessary to introduce different concentrations of hydrogen sulfide and nitric oxide gases into the carbon monoxide electrochemical element under standard experimental conditions, measure the concentration of the carbon monoxide electrochemical element, obtain the cross-interference coefficient, and then program the sensor. In this way, the carbon monoxide gas concentration in automotive exhaust environments can be accurately measured.

To study the gas cross-interference algorithm, the carbon monoxide sensor as a whole was first subjected to gas concentration measurement experiments to obtain test data. Then, the variation patterns were analyzed, and empirical mathematical formulas were used to compensate for gas cross-interference. Firstly, three prototypes are selected and the accuracy of the carbon monoxide sensor is calibrated using a carbon monoxide standard gas with a concentration of 500 ppm at 25 °C. Then, the initial concentration of carbon monoxide gas is measured. If the displayed value of the sensor is not 500 ppm at this time, calibrate the sensor to 500 ppm. Inject 100 ppm hydrogen sulfide gas, calibrate the sensor's hydrogen sulfide gas detection value to 100 ppm, read the measurement values of the carbon monoxide hydrogen sulfide dual gas and nitric oxide detection modules, and record the measurement values of the three sensors. The recorded data are shown in Table 1.

From Table 1, it can be seen that when 100 ppm hydrogen sulfide gas is introduced, both the carbon monoxide and hydrogen sulfide signal channels of the carbon monoxide and hydrogen sulfide dual gas detection module exhibit signal changes. The average of the measured carbon monoxide concentrations of the three sensor prototypes is 20.33 ppm, so the cross-interference

Table 1  
Measured concentration using a 100 ppm hydrogen sulfide gas sensor detection module in a laboratory environment at 25 °C.

Prototype no.	Measured concentration of carbon monoxide (ppm)	Measured concentration of hydrogen sulfide (ppm)	Measured concentration of nitric oxide (ppm)
1#	21	100	2
2#	20	100	2
3#	20	100	3



coefficient in Eq. (1) is 0.2033. When 100 ppm hydrogen sulfide gas is introduced, the measured value of the nitric oxide detection module is not greater than 3 ppm, indicating that the cross-interference of hydrogen sulfide gas on the nitric oxide detection module is small and can be ignored.

Nitric oxide gas (100 ppm) is injected and the sensor's detection value of the nitric oxide gas is calibrated to 100 ppm. Then, the measurement values are read from the carbon monoxide hydrogen sulfide dual gas and nitric oxide detection modules. Lastly, the measurement values of three sensors are recorded. The data are shown in Table 2.

From Table 2, it can be seen that when 100 ppm nitric oxide gas is introduced, there is a signal change in the carbon monoxide signal channel of the carbon monoxide hydrogen sulfide dual gas detection module, while there is almost no signal change in the hydrogen sulfide signal channel. This indicates that the cross-interference of nitric oxide gas on the detection of hydrogen sulfide gas is relatively small and can be ignored. The average measured concentration of carbon monoxide for the three sensor prototypes is 27.67 ppm; therefore, the cross-interference coefficient in Eq. (1) is 0.2767.

Therefore, under standard experimental conditions, different concentrations of hydrogen sulfide and nitric oxide gases were introduced into the carbon monoxide electrochemical element, and the cross-interference coefficient was obtained. The actual concentration of carbon monoxide gas calculated using Eq. (1) is as follows.

$$A_1 = A_0 - 0.2767 \times C_0 - 0.2033 \times B_0 \quad (2)$$

We use C language to program the calculation logic of Eq. (2) as the gas concentration cross interference calculation function in the microcontroller logic program on the sensor motherboard. During the sensor detection process, the sensors sequentially detect the concentrations of carbon monoxide, hydrogen sulfide, and nitric oxide gases. Then, by calculating the cross interference function of gas concentration, the cross-interference of hydrogen sulfide and nitric oxide gases is eliminated, achieving an accurate measurement of carbon monoxide gas concentration in the automotive exhaust environment.

## 5. Results and Discussion

At present, the mainstream carbon monoxide sensors in the market, including sensor products produced by companies such as City Technology Limited in the UK and Alpha Sense in the UK,

Table 2  
Measured concentration using a 100 ppm nitric oxide gas sensor detection module in a laboratory environment at 25 °C.

Prototype no.	Measured concentration of carbon monoxide (ppm)	Measured concentration of hydrogen sulfide (ppm)	Measured concentration of nitric oxide (ppm)
1#	28	0	100
2#	27	1	100
3#	28	1	100

which all have the problem of gas cross-interference, adopt the electrochemical detection principle. To verify the feasibility of the gas detection module and gas cross-interference algorithm based on composite electrochemical components, as well as the accuracy of detecting the carbon monoxide gas concentration in mixed gas environments, a carbon monoxide sensor gas detection module sample based on composite electrochemical components was made. The detection circuits of the carbon monoxide hydrogen sulfide dual gas and nitric oxide detection modules were designed on the same circuit board. The sensitive components are GS+4DT and GS+4NO. A photograph of the sample is shown in Fig. 7.

A mixed standard gas sample with 500 ppm carbon monoxide, 100 ppm nitric oxide, and 100 ppm hydrogen sulfide is configured for testing. The remaining components are air. Three sensor prototypes are fabricated, and their accuracies are first calibrated. Then, the configured standard gas is allowed to pass the three prototypes and the measurement concentrations of carbon monoxide, hydrogen sulfide, and nitric oxide gases are read from the sensors and recorded. The recorded data are shown in Table 3.

According to the basic performance parameters in Table 3, the developed carbon monoxide sensor based on composite electrochemical components has a measurement error of less than 5% in mixed gas environments, meeting the industry standard requirements of AQ6205-2006 mining carbon monoxide sensors.

To facilitate the promotion and application of the developed carbon monoxide sensor in coal mines, it is necessary to entrust a qualified inspection agency to conduct spark ignition tests and the evaluation of the sensor in accordance with the “ia” protection level in GB3836.4-2021.



Fig. 7. (Color online) Fabricated gas detection module for carbon monoxide sensor based on composite electrochemical components.

Table 3

Gas concentrations measured by the sensor when the mixed gas is introduced in the laboratory environment.

Prototype no.	Measured value of carbon monoxide (ppm)	Measured value of hydrogen sulfide (ppm)	Measured value of nitric oxide (ppm)
1#	513	97	98
2#	495	101	96
3#	507	98	98

## 6. Conclusions

We adopted a carbon monoxide gas concentration detection technology based on composite electrochemical components, integrating the detection circuits of the carbon monoxide hydrogen sulfide dual gas and nitric oxide detection modules to achieve the multicomponent composite detection of carbon monoxide, hydrogen sulfide, and nitric oxide gases. Then, by the cross-interference compensation method, the effects of hydrogen sulfide and nitric oxide gases on the detection of carbon monoxide gas concentration were eliminated, solving the problem of the impact of exhaust and sulfur-containing gases from underground rubber-tire vehicles on the accuracy of carbon monoxide gas detection. Furthermore, the gas cross-interference error was within 5%, and the accurate detection of carbon monoxide gas was achieved. The carbon monoxide sensor developed in this study based on composite electrochemical components has low power consumption, small gas cross-interference, and good stability. It is of great significance in the detection of characteristic gases in coal mine fires and is suitable for the complex working conditions in coal mines. It has broad prospects for promotion and application.

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