Accurate Concentration Measurement Model of Multicomponent Mixed Gases during a Mine Disaster Period

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ABSTRACT: A variety of gaseous products are formed when mine fires and coal and gas outbursts occur in mines. On the one hand, these gas products affect the normal production of mines and the occupational health of miners; on the other hand, the gaseous products can also provide much important information to prevent mine disasters. Thus, the rapid and accurate determination of the component content of multicomponent mixed gases is of great significance. However, the distortion of gas chromatography measurement results, which deviate from the true values, has a serious impact on gas composition determination in mines. To reduce the influence of distortion, an Agilent 490 portable gas chromatograph is used to measure the component content of 11 groups of standard multicomponent mixed gases. It is found that the error rate of the measured result is highly related to the concentration of the selected reference component and the component to be measured. Besides, the key point of each gas concentration is determined according to the scatter diagram of the error rate. Each gas is divided into a high and a low concentration group by the key points, and each gas is selected as the reference component to measure the corresponding component concentration in other gases with multiple-point external standards. Researchers have used the least-squares method to fit univariate linear regression analysis between the measured values and true values of mixed gases. Then, the optimal analysis function and the optimal reference component concentration of each gas can be determined by comparing the regression analysis parameters. Finally, it is found that the error rate of measured values corrected by the optimal analysis function is significantly reduced. It is proved that this method can effectively alleviate the measurement results’ distortion, which solves the problem of gas composition determination in underground areas.

1. INTRODUCTION

Coal is the most abundant fossil resource on the earth. The issue of safety in mining not only affects the normal production of coal mines but also seriously restricts the development of major coal-producing countries such as China, Poland, the United States, Australia, and so on. In mine disasters, mine fires, and coal and gas outbursts, fire damp explosion often occurs in mines, which not only causes casualties and losses of property but also leads to serious social problems. Mine fires are mostly caused by coal spontaneous combustion (CSC). CSC is caused by coal oxidation, and the oxidation process is supported by the ability of coal to absorb oxygen, with the simultaneous release of heat.
If the heat production rate from the oxidation reaction exceeds the rate of cooling by ventilation or the environment, the temperature will continue to rise. When coal exceeds its critical temperature, it will lead to CSC left in active or sealed longwall. The temperature will continue to rise. When coal exceeds its critical temperature, it will lead to CSC left in active or sealed longwall. When coal exceeds its critical temperature, it will lead to CSC left in active or sealed longwall. When coal exceeds its critical temperature, it will lead to CSC left in active or sealed longwall.

During the oxidation process, unstable functional groups, bridge bonds, and radicals are separated from the coal macromolecular structure to form many gaseous products (such as CO, H₂, CO₂, CH₄, C₂H₆, C₂H₄, C₂H₂, and C₃H₄). These gaseous products reveal important information on CSC; CO is the first gas generated in these gases, which has a clear corresponding relationship with the coal oxidation temperature. Therefore, CO is used as an index gas for predicting CSC in many countries. Xu explored the reaction mechanism of free radicals and functional groups during low-temperature oxidation of coal and the law of active groups producing CO. Jiang analyzed the mechanism of the effect of gas atmosphere conversion on the radical reaction and CO generation rate. Many scholars used other gaseous products (CO₂, C₂H₆, C₂H₄, C₂H₂, etc.) as single-index gases to determine the development state of CSC. Although it is more convenient to calculate with single-index gases, this method is influenced by fresh air. Thus, composite index gases have been proposed. Hu used composite index gases to analyze drained gas in the upper tunnel, which provides an assessment of CSC in gob. Miao introduced higher-molecular-weight gases to address the blank prediction interval of conventional composite index gases when predicting CSC. Kuchta’s research pointed out that if fire cannot be extinguished within 2 h, the fire area should be closed immediately. The flow decrease in the closed fire zone, which is prone to gas accumulation, can lead to gas explosion and secondary disaster. The US Bureau of Mines studied the variation law of indicator gases in closed fire zones and proposed the explosion triangle method to calculate the explosion risk of combustible gases. Zhou determined the explosion area triangle of the methane explosion limit and the oxygen volume fraction by studying the temperature, pressure, combustible gas, and inert gas concentration in a closed fire zone. Zhou proposed a multiparameter judgment method and related the safety factor model for unsealing the fire area using the BP neural network according to the variation characteristics of index gases. These research results have proved that accurate determination of the component content of multicomponent mixed gases is valuable for understanding the process of fire extinguishment and guiding the fire area unsealing in a closed fire zone.

In addition, an abundance of toxic gases is produced when coal and gas outbursts as well as fire damp explosions occur in mines. These toxic gases not only can cause casualties (such as CO directly inhibits intracellular respiration and causes severe hypoxia in human tissue cells, resulting in damage to the central nervous system and cardiovascular system if miners are exposed to an environment with a high concentration of CO for a long time) but also can move to other tunnels to induce secondary disaster (such as fire damp explosion and gas suffocation). Scholars have studied the distribution of gas concentration after mine gas accidents. Liu divided the propagation of poisonous gases after a fire damp explosion into three stages and established a calculation model for the propagation of poisonous gases in a tunnel. Jia improved the Gaussian puff model according to the actual situation of poisonous gas diffusion and obtained the law of poisonous gas diffusion suitable for fire damp explosion. The concentration distribution of these toxic gases not only affects the safety of site miners but also has an important influence on rescue work. According to the “Coal Mine Safety Regulations”, after a disaster accident occurs in a mine, mine rescue teams must first be organized to conduct reconnaissance of the disaster area. Due to the complex safety situation of coal mines in China, it is necessary to constantly strengthen the mine rescue teams. There have been 463 full-time coal mine rescue teams, including more than 30 000 commanders and fighters. A large number of rescuers also sacrificed their lives because of the limitation of monitoring technology and equipment. Since 1960, there have been more than 280 accidents in emergency rescue work, and nearly 600 mine emergency rescue fighters have died in mine accidents. Among the casualties, explosion accidents accounted for 46%, poisoning accidents accounted for 33.9%, and suffocation accidents accounted for 10.5%. The main reason for these rescue casualties is the unclear understanding of the concentration of multicomponent mixed gases. It shows that the accurate determination of multicomponent mixed gases plays a vital role in emergency rescue work after gas disasters in mines.

To address the problems caused by unknown gaseous products’ concentration, the requirements for quantitative analysis technology have been continuously developed. Quantitative analysis can be divided into chemical analysis and instrumental analysis to determine the amount of multicomponent mixed gases. Chemical analysis is complicated and susceptible to the interference and influence of system random error. Instrumental analysis indirectly reflects the concentration of a substance by the physical properties, such as conductivity, electrode potential, light absorption or emission, mass-to-charge abundance, and fluorescence. Thus, gas detectors can be divided into flame ionization, electron capture, photoionization detector, Fourier-transform infrared spectrometry, X-ray fluorescence spectrometry, mass spectrometry, gas chromatography (GC), and so on according to the different physical properties. However, most of these instruments are single-parameter detection equipment, where the detection object is a single gas. Thus, these instruments are insufficient to deal with multicomponent mixed gases. In contrast, GC has the advantages of being able to simultaneously detect multiple gases, having a high separation efficiency for complex mixed substances, and possessing a fast processing speed, simple operation, high quality, and low price. However, when GC is used to detect mixed gases, it leads to loss of target compounds and cross-contamination, affecting the results. According to the GC measurement results of the Xuanzong and Liuguantun coal mine in 2006, as shown in Table 1, it was found that the distortion of GC measurement results, which is the sum of component concentrations, severely deviated from 100%. Combined with the above, measuring the mixed-gas concentration accurately plays an important role in preventing CSC and coal and gas outbursts, and hence the distortion of GC measurement results leads to serious trouble in fire extinguishment, the fire area unsealing in a closed fire zone, and emergency rescue work in coal mines. The reason for distortion is that GC cannot make an accurate qualitative judgment on a general unknown system. It can only make more accurate qualitative judgments for systems for which we have prior information on their outline. Thus, calibration is essential to measure the response generated from a sample composed of a known amount of analyte prior to determination of the unknown. At present, there are several types of quantitative methods commonly used, including area percent, single-point external standard, multiple-
2. EXPERIMENTAL SETUP AND SAMPLE PREPARATION

2.1. Experimental Setup. GC has great advantages and is widely used in determining the composition and concentration of multicomponent mixed gases. In this paper, the Agilent 490 portable gas chromatograph (Agilent 490GC) has been used to test the component concentration of the multicomponent mixed standard gases.

The Agilent 490GC is composed of four independent chromatographic column channels: micro-GC, electronic carrier gas control, a micro-machine sampler, a narrow-bore analytical column, and a micro thermal conductivity detector. The narrow-diameter capillary is used to measure gas components, greatly reducing the measurement time. The four independent analysis GC channels can be flexibly used in various environments and can be quickly reconfigured for different application conditions. In addition, the instrument can avoid the interference of other gases in the external environment through a microelectronic gas control device and an optional time-programmed backflush device. The physical diagram of Agilent 490GC is shown in Figure 1, the instrument test flow diagram is shown in Figure 2, and the measurement parameter settings are shown in Table 2.

2.2. Preparation of Multicomponent Mixed-Gas Samples. To comprehensively simulate the composition of harmful gases in different mine disaster periods and avoid the deviation of the GC test results due to the instability of gases, this research uses multicomponent mixed gases with N2, O2, CH4, CO, CO2, C2H4, C2H6, C2H2, and C3H8. These gases meet the national first-class gas standard; the composition and concentration of the 11 groups of multicomponent mixed gas samples are shown in Table 3.

2.3. Reliability and Stability Test of Experimental Instrument. Before the component content determination experiment of the multicomponent mixed gas, the performance of the Agilent 490GC was tested to avoid large deviation in the measured results caused by instrumentation errors. The relative standard deviation of the gas peak area response value is determined by the multicomponent mixed gases 2# and 6#. The relative standard deviation of the measurement results is 0.06–0.9% and none of them exceeds 3%, as can be seen from Table 4 and Table 5. The measurement results meet the requirements of the JJG700-2019 “Gas Chromatograph Verification Regula-

Table 1. Measurement Results of Fire Gas Concentration in Xuandong and Liuguantun Coal Mines in 2006

| gas composition | Xuandong coal mine 1# | Xuandong coal mine 2# | Liuguantun coal mine 3# | Liuguantun coal mine 4# |
|-----------------|-----------------------|-----------------------|-------------------------|-------------------------|
| He              | 0.0006                | 0.0004                | 0.0012                  | 0.0007                  |
| H2              | 0.7857                | 0.7715                | 2.0708                  | 1.1803                  |
| O2              | 11.7948               | 10.3149               | 11.6356                 | 14.6132                 |
| N2              | 84.9099               | 84.4297               | 68.3043                 | 71.8538                 |
| CH4             | 3.5739                | 5.8736                | 0.4904                  | 0.2517                  |
| CO              | 0.3947                | 0.4179                | 2.165553                | 1.15708                 |
| CO2             | 5.5677                | 6.4891                | 5.7062                  | 3.5089                  |
| C2H4            | 0.0167                | 0.0274                | 0.032399                | 0.016296                |
| C2H6            | 0.2482                | 0.3147                | 0.038314                | 0.019584                |
| C2H2            | 0.0205                | 0.0023                | 0                  | 0                      |
| C3H8            | 107.31                | 108.64                | 90.44                   | 92.6                   |

Figure 1. Physical diagram of Agilent 490 portable gas chromatograph (reprinted in part with permission from the user manual for the Agilent 490 portable gas chromatograph G3581-97001. Copyright 2017 Agilent Technologies, Inc.).
tions”, so the Agilent 490GC has stable performance and strong reliability and meets the accuracy requirements.

3. EXPERIMENTAL PROTOCOL

In this paper, the composition and concentration of a standard multicomponent mixed gas are determined by Agilent 490GC. First, a specific gas (H₂, O₂, CH₄, etc.) in a set of standard gas samples (1#−11#) is selected as a reference component. Second, GC is used to measure the concentration of this component in other gas samples to obtain the response result. Third, this component in another standard gas sample is used as the reference component, and then, the concentration is measured in other gas samples. Finally, this kind of test is considered complete when this component in all gas samples is used as the reference component. Similarly, the concentration of another component is measured with this method. The response of reference components with different concentrations and types is obtained by GC. Finally, the response function between the measured results and the true concentration of different types and concentrations are established.

The specific operations for determining the components in the mixed gases are as follows: turn on the GC $\rightarrow$ preheat the instrument $\rightarrow$ select the standard gas $\rightarrow$ measure the standard gas $\rightarrow$ calibrate the standard gas sample $\rightarrow$ measure the gas concentrations of other groups; measure the various gas concentrations of each group in turn and analyze the measured results.

During the experiment, the measurement environment was as follows: 25°C and 65 ± 15% RH. To reduce the influence of residual gases, the same group of gas was measured 3 times, and the last measurement result was used.

4. EXPERIMENTAL RESULTS AND ANALYSES

We selected H₂, O₂, CH₄, CO, CO₂, C₂H₄, C₂H₆, and C₃H₈ in turn, set the component as the reference component, and used GC to measure the concentration of this component in other standard gas samples. The measurement results of this gas

![Figure 2. Test flow diagram of the Agilent 490 portable gas chromatograph.](https://doi.org/10.1021/acsomega.2c02391)

### Table 2. Agilent 490MicroGC Portable Gas Chromatograph Measurement Parameter Setting Table

| aisle | carrier gas | column temperature (°C) | injection time (ms) | running time (s) | cylinder head pressure (kPa) | backflush time (s) |
|-------|-------------|--------------------------|---------------------|-----------------|-----------------------------|-------------------|
| A     | He          | 60                       | 70                  | 120             | 180                         | 5                 |
| B     | He          | 60                       | 120                 | 120             | 180                         | 8                 |

![Table 3. Multicomponent Mixed-Gas Component Concentration Table (Unit: %)](https://doi.org/10.1021/acsomega.2c02391)

| gas number | H₂  | O₂  | N₂  | CH₄ | CO  | CO₂ | C₂H₄ | C₂H₆ | C₃H₈ |
|------------|-----|-----|-----|-----|-----|-----|-------|-------|-------|
| 1#         | 0.00928 | 0.509 | 7.38822 | 89.9 | 1.84 | 0.101 | 0 | 0.186 | 0.0665 | 0 |
| 2#         | 5.96 | 1 | 20.65 | 60 | 1.93 | 10 | 0.156 | 0.198 | 0.0809 | 0.0251 |
| 3#         | 0.0532 | 1.92 | 16.6927 | 79.3 | 1.53 | 0.249 | 0.00483 | 0.167 | 0.0557 | 0.0276 |
| 4#         | 4 | 3.08 | 46.6834 | 29.9 | 1.04 | 15 | 0.0811 | 0.154 | 0.041 | 0.0205 |
| 5#         | 0.104 | 3.65 | 23.7356 | 70.4 | 1.36 | 0.5 | 0.0305 | 0.135 | 0.052 | 0.0329 |
| 6#         | 2.03 | 5 | 52.3899 | 15.1 | 0.497 | 24.8 | 0.0417 | 0.106 | 0.0203 | 0.0151 |
| 7#         | 0.494 | 5.4 | 41.4424 | 50.2 | 1.24 | 0.963 | 0.0513 | 0.125 | 0.0463 | 0.038 |
| 8#         | 1.38 | 6.53 | 47.9965 | 40.4 | 1.07 | 2.39 | 0.061 | 0.0898 | 0.0407 | 0.042 |
| 9#         | 0.506 | 15.1 | 76.7847 | 2.5 | 0.0996 | 4.92 | 0.0199 | 0.05 | 0.00993 | 0.00991 |
| 10#        | 0 | 17.4 | 59.815 | 0.0979 | 0.0504 | 22.4 | 0.16 | 0.00465 | 0 | 0.0721 |
| 11#        | 0.0998 | 20.1 | 78.2746 | 0.986 | 0.0101 | 0 | 0.00998 | 0.00953 | 0.00502 | 0.00494 |
determined under different concentration reference components are obtained.

4.1. Analysis of H₂ Measured Results. We set H₂ in standard mixed gases 1#–9# and 11# as the reference component (the H₂ concentration of 10# is 0) and measured the H₂ concentration in other gas samples. From Table 6, it can be seen that the measured values deviate from the true values when we use different concentrations of H₂ reference components. To accurately measure the deviation between the measured value and the true value under different concen-
Figure 3. Scatter diagram of the measurement error rate of the H\textsubscript{2} content in each group of mixed gases under different concentrations of reference substances. (a) Measurement error rate of gas 1\# with the concentration of 0.00928\% at different concentrations of the reference component. (b) Measurement error rate of gas 2\# with the concentration of 5.96\% at different concentrations of the reference component. (c) Measurement error rate of gas 3\# with the concentration of 0.0532\% at different concentrations of the reference component. (d) Measurement error rate of gas 4\# with the concentration of 4\% at different concentrations of the reference component. (e) Measurement error rate of gas 5\# with the concentration of 0.104\% at different concentrations of the reference component. (f) Measurement error rate of gas 6\# with the concentration of 2.03\% at different concentrations of the reference component. (g) Measurement error rate of gas 7\# with the concentration of 0.494\% at different concentrations of the reference component. (h) Measurement error rate of gas 8\# with the concentration of 1.38\% at different concentrations of the reference component. (i) Measurement error rate of gas 9\# with the concentration of 0.506\% at different concentrations of the reference component. (j) Measurement error rate of gas 10\# with the concentration of 0.0998\% at different concentrations of the reference component.
treated by the following formula

\[ \eta = \frac{a - b}{b} \]  

(1)

where \( a \) is the true concentration of \( H_2 \) in the standard gas sample, \( b \) is the measured value under different reference components, and \( \eta \) is the error rate of the measured value.

The error rate between the measured value and the true value of \( H_2 \) in other standard gas samples is shown in Table 7. It is found that the error rate of the measured value varies greatly with different concentrations of \( H_2 \) reference components. For example, the true concentration of \( H_2 \) in standard gas sample 1# is 0.00928%; when the standard gas sample 2# is chosen as the reference component (the \( H_2 \) concentration of 2# is 5.96%), the 1# measured value is 0.015434% and the error rate is as high as 0.663. However, when the standard gas sample 5# is chosen as the reference component (the \( H_2 \) concentration of 5# is 0.104%), the result is 0.00821%, with an error rate as low as 0.115.

It is found that the main influencing factors causing the error rate of the \( H_2 \) measured value are (1) the gas component to be measured, \( H_2 \) concentration, and (2) \( H_2 \) reference component concentration. To clear the trend of the error rate, the scatter diagram of 10 groups’ standard mixed gases (1#—9#, 11#) under different concentrations of \( H_2 \) reference components is fitted in Figure 3. It is seen from Figure 3 that the error rate of the \( H_2 \) concentration measurement varies with the concentration of the \( H_2 \) reference component. The 10 kinds of standard gas samples can be divided into two categories according to the variation trend of the measured value error rate. (1) The gas samples represented in Figure 3a, 3c, 3e, 3g, 3i are classified as group A. When using a low-concentration \( H_2 \) reference component, the error rate of the measured value in this group is low. (2) The gas samples represented in Figure 3b, 3d, 3f, 3h, 3j are classified into group B, when the concentration of the selected reference component is too high, the concentration difference between the reference component and group A becomes too large. There is a big deviation between the result of GC and the true value. For group B, when the high-concentration \( H_2 \) reference component is selected for measurements, the error rate of measurement results is low. However, when the concentration of the selected reference component is too high, the concentration difference between the reference component and group A becomes too large. Therefore, selecting the appropriate concentration of reference components can effectively reduce the measurement error rate.

Based on Figure 3, the key point for the error rate of \( H_2 \) concentration determination is 0.506%. Hence, group A, where the \( H_2 \) concentration less than 0.506%, is called the low-concentration \( H_2 \) gas, and group B, where the \( H_2 \) concentration is greater than or equal to 0.506%, is called the high-concentration \( H_2 \) gas. The response characteristics of GC with different \( H_2 \) concentration ranges are determined, and then, the optimal response function of GC in different \( H_2 \) concentration ranges is obtained by comparing the response characteristic parameters.

Because the concentration of \( H_2 \) reference components has a great influence on the measured results, the measured values and the true values of \( H_2 \) in group A are fitted by linear regression when the low-concentration \( H_2 \) is selected as the reference component, as shown in Figure 4a. At the same time, we set the confidence level of the univariate linear regression fitting as 95%, and the coefficient of determination (\( r^2 \)) and the residual sum of squares (SSe) of the fitting model are calculated. When the \( r^2 \) is closer to 1 and the SSe is closer to 0, the effect of univariate linear

\[ r^2 \]  

(2)

The \( H_2 \) concentration values in group A are 0.00928, 0.0532, 0.104, 0.494, and 0.0998%; the \( H_2 \) concentration values in group B are 5.96, 4, 2.03, 1.38, and 0.506%. The \( H_2 \) concentration values in group B are much higher than those in group A. For group A, when the low-concentration \( H_2 \) reference component is selected for measurements, the GC can accurately measure the concentration of \( H_2 \). However, when the concentration of the selected reference component is too high, the concentration difference between the reference component and group A becomes too large. There is a big deviation between the result of GC and the true value. For group B, when the high-concentration \( H_2 \) reference component is selected for measurements, the error rate of measurement results is low. However, when the concentration of the selected reference component is too high, the concentration difference between the reference component and group A becomes too large. Therefore, selecting the appropriate concentration of reference components can effectively reduce the measurement error rate.

Table 8. Low-Concentration \( H_2 \) Univariate Linear Regression Analysis Parameter Table

| Fit metrics                     | Reference 1# | Reference 3# | Reference 5# | Reference 7# | Reference 11# |
|---------------------------------|--------------|--------------|--------------|--------------|--------------|
| Coefficient of determination (r²) | 0.994937     | 0.977738     | 0.98389      | 0.902635     | 0.994204     |
| Residual sum of squares (SSe)   | 0.000519     | 0.004875     | 0.00214      | 0.000558     | 0.000765     |

Figure 4. Fitting graph of the univariate linear regression between the measured concentration of \( H_2 \) and the true concentration in different concentration intervals. (a) Low-concentration \( H_2 \) measured and true value univariate linear regression fitting plot. (b) High-concentration \( H_2 \) measured and true value univariate linear regression fitting plot.
regression analysis is better, and the corresponding fitting function is the optimal analysis function. Comparing the regression analysis parameters of group A (1#, 3#, 5#, 7#, 11#) in Table 8, it is found that when using gas 1# as the reference component, the regression analysis effect is found to be the best, and the fitting function is the optimal analysis function for the determination of low-concentration H₂.

When the high concentration of H₂ was chosen as the reference component, fitting the H₁ measured values and true values of group B as shown in Figure 4b. Through comparing the regression analysis parameters of group B (2#, 4#, 6#, 8#, 9#) in Table 9, when using gas 4# as the reference component, the regression analysis effect is found to be the best, and the fitting function is the optimal analysis function.

Therefore, when measuring low-concentration H₂ in the normal period of mines, standard gas sample 1# (the H₂ concentration is 0.00928%) is selected as the reference component. When measuring high-concentration H₂ during the disaster period, standard gas sample 4# (the H₂ concentration is 4%) is selected as the reference component.

The optimal analysis function of GC in different H₂ concentration ranges is

\[
y = 1.1778x - 0.000177, x < 0.506% \\
y = 1.0793x - 0.001958, x \geq 0.506% 
\]  

(2)

4.2. Analysis of O₂ Measured Results. We set O₂ in standard mixed gases 1#–11# as the reference component and measure the O₂ concentration in other gas groups. Due to the large amount of O₂ concentration (the actual O₂ concentration is 0.509–20.1%), the measured error of O₂ concentration is large. Similarly, the key point for the error rate of the O₂ concentration determination is 5%. The response characteristics of low-concentration O₂ gases are determined by the reference components with concentrations less than 5%, and the optimal response function of GC is determined in this concentration range. By the same method, the optimal response function of the high-concentration O₂ standard gas sample is determined using the reference component of the O₂ concentration greater than or equal to 5%.

The gas samples with low-concentration O₂ (1#, 2#, 3#, 4#, 5#) are classified as group C, and the gas samples with high-concentration O₂ (6#, 7#, 8#, 9#, 10#, 11#) are classified as group D. Setting the confidence level of the univariate linear regression fitting as 95%, the optimal analysis function is obtained by performing univariate linear regression analysis between the measured value and the true value of O₂ in different concentration ranges.

Figure 5 shows the fitting results of the univariate linear regression between the measured values and the true values of O₂. When measuring the group C gases, which represent the low-concentration O₂ during a disaster period in mines, gas sample 3# (the O₂ concentration is 1.92%) is used as the reference component. When measuring the group D gases, which represent the high-concentration O₂ during a normal period in mines, gas sample 6# (the O₂ concentration is 5%) is used as the reference component, and the univariate linear regression analysis effect is found to be the best. From this, the optimal analysis function of the GC in different O₂ concentration ranges is

\[
y = 1.3079x - 0.002356, x < 5% \\
y = 1.2127x - 0.015983, x \geq 5% 
\]  

(3)

4.3. Analysis of CH₄ Measured Results. The key point for the error rate of the CH₄ concentration determination is 40.4%. The response characteristics of low-concentration CH₄ gases are determined by reference components with concentration less than 40.4%, and then, the optimal response function of GC is determined in this concentration range. By the same method, the optimal response function of high-concentration CH₄ standard gas samples is determined using the reference component of CH₄ concentration greater than or equal to 40.4%. The gas samples with low-concentration CH₄ (4#, 6#, 9#, 10#, 11#) are classified as group E, and the gas samples with high-concentration CH₄ (1#, 2#, 3#, 5#, 7#, 8#) are classified as

Table 9. High-Concentration H₂ Univariate Linear Regression Analysis Parameter Table

| fit metrics                  | reference 2# | reference 4# | reference 6# | reference 8# | reference 9# |
|-----------------------------|-------------|-------------|-------------|-------------|-------------|
| coefficient of determination | 0.998646    | 0.999342    | 0.996652    | 0.998753    | 0.995988    |
| residual sum of squares (SSₑ) | 0.008956    | 0.011466    | 0.062266    | 0.021032    | 0.014932    |
group F. Finally, the optimal analysis function is obtained by performing univariate linear regression analysis between the measured value and the true value of CH$_4$ in different concentration ranges.

**Figure 6** shows the fitting results of the univariate linear regression with different CH$_4$ concentration ranges. When measuring the group E gases, which represent the low-concentration CH$_4$ in the normal period, gas sample 6$^\#$ (the CH$_4$ concentration is 15.1$\%$) is used as the reference component. When measuring the group F gases, which represent the high-concentration CH$_4$ during a disaster period, gas sample 1$^\#$ (the CH$_4$ concentration is 89.9$\%$) is used as the reference component. On this basis, the univariate linear regression analysis effect between the measured values and the true value is found to be the best. From this, the optimal analysis function of the GC in different CH$_4$ concentration ranges is

$$y = 0.9821x - 0.000216, \quad x < 40.4\%$$  
$$y = 1.0949x - 0.013066, \quad x \geq 40.4\%$$  

**4.4. Analysis of CO Measured Results.** The key point for the error rate of the CO concentration determination is 1.24$.\%$. The response characteristics of low-concentration CO gases are determined by reference components with concentration less than 1.24$,\%$, and then, the optimal response function of GC is determined in this concentration range. By the same method, the optimal response function of high-concentration CO standard gas samples is determined using the reference component of the CO concentration greater than or equal to 1.24$.\%$. The gas samples with low-concentration CO (4$^\#$, 6$^\#$, 8$^\#$, 9$^\#$, 10$^\#$, 11$^\#$) are classified as group G, and the gas samples with high-concentration CO (1$^\#$, 2$^\#$, 3$^\#$, 5$^\#$, 7$^\#$) are classified as group H. Finally, the optimal analysis function is obtained by performing univariate linear regression analysis between the measured value and the true value of CO in different concentration ranges.

**Figure 7** shows the fitting results of the univariate linear regression with different CO concentration ranges. When measuring the group G gases, which represent the low-concentration CO in the normal period, gas sample 6$^\#$ (the CO concentration is 0.497$\%$) is used as the reference component. When measuring the group F gases, which represent the high-concentration CO during a disaster period, gas sample 1$^\#$ (the CO concentration is 1.84$\%$) is used as the reference component. On this basis, the univariate linear regression analysis effect between the measured values and the true value was found to be the best. From this, the optimal analysis function of the GC in different CO concentration ranges is found to be
Analysis of CO\textsubscript{2} Measured Results. The key point for the error rate of the CO\textsubscript{2} concentration determination is 2.39\%. The response characteristics of low-concentration CO\textsubscript{2} gases are determined by reference components with concentration less than 2.39\%, and then, the optimal response function of GC is determined in this concentration range. By the same method, the optimal response function of high-concentration CO\textsubscript{2} standard gas samples is determined using the reference component of CO\textsubscript{2} concentration greater than or equal to 2.39\%. The gas samples with low-concentration CO\textsubscript{2} (1\#, 3\#, 5\#, 7\#) are classified as group I, and the gas samples with high-concentration CO\textsubscript{2} (2\#, 4\#, 6\#, 8\#, 9\#, 10\#) are classified as group J. Finally, the optimal analysis function is obtained by performing univariate linear regression analysis between the measured value and the true value of CO\textsubscript{2} in different concentration ranges.

Figure 8 shows the fitting results of the univariate linear regression with different CO\textsubscript{2} concentration ranges. When measuring the group I gases, which represent the low-concentration CO\textsubscript{2} in the normal period, gas sample 1\# (the CO\textsubscript{2} concentration is 0.101\%) is used as the reference component. When measuring the group J gases, which represent the high-concentration CO\textsubscript{2} during the disaster period, gas sample 10\# (the CO\textsubscript{2} concentration is 22.4\%) is used as the reference component. On this basis, the univariate linear regression analysis effect between the measured values and the true value is found to be the best. From this, the optimal analysis function of the GC in different CO\textsubscript{2} concentration ranges is

\[
\begin{align*}
y &= 0.9734x + 0.000959, \quad x < 1.24\% \\
y &= 0.8781x + 0.002438, \quad x \geq 1.24\% 
\end{align*}
\]

**Figure 8.** Fitting diagram of univariate linear regression between the measured concentration of CO\textsubscript{2} and the true concentration in different concentration intervals. (a) Low-concentration CO\textsubscript{2} measured and true value univariate linear regression fitting plot. (b) High-concentration CO\textsubscript{2} measured and true value univariate linear regression fitting plot.

4.6. Analysis of C\textsubscript{2}H\textsubscript{4} Measured Results. The key point for the error rate of the C\textsubscript{2}H\textsubscript{4} concentration determination is 0.061\%. The response characteristics of low-concentration C\textsubscript{2}H\textsubscript{4} gases are determined by reference components with concentration less than 0.061\%, and then, the optimal response function of GC is determined in this concentration range. By the same method, the optimal response function of high-concentration C\textsubscript{2}H\textsubscript{4} standard gas samples is determined using the reference component of the C\textsubscript{2}H\textsubscript{4} concentration greater than or equal to 0.061\%. The gas samples with low-concentration C\textsubscript{2}H\textsubscript{4} (3\#, 5\#, 6\#, 7\#, 9\#, 11\#) are classified as group K, and the gas samples with high-concentration C\textsubscript{2}H\textsubscript{4} (2\#, 4\#, 8\#, 10\#) are classified as group L. Finally, the optimal analysis function is obtained by performing univariate linear regression analysis
between the measured value and the true value of \( \text{C}_2\text{H}_4 \) in different concentration ranges.

Figure 9 shows the fitting results of the univariate linear regression with different \( \text{C}_2\text{H}_4 \) concentration ranges. When measuring the group K gases, which represent the low-concentration \( \text{C}_2\text{H}_4 \) in the normal period, gas sample 11\# (the \( \text{C}_2\text{H}_4 \) concentration is 0.00998\%) is used as the reference component. When measuring the group L gases, which represent the high-concentration \( \text{C}_2\text{H}_4 \) during the disaster period, gas sample 2\# (the \( \text{C}_2\text{H}_4 \) concentration is 0.156\%) is used as the reference component. On this basis, the univariate linear regression analysis effect between the measured values and the true value is found to be the best. From this, the optimal analysis function of the GC in different \( \text{C}_2\text{H}_4 \) concentration ranges is

\[
y = 0.9053x + 0.000005, \quad x < 0.061\% \\
y = 1.0568x + 0.000024, \quad x \geq 0.061\% \tag{7}
\]

4.7. Analysis of \( \text{C}_2\text{H}_6 \) Measured Results. The key point for the error rate of the \( \text{C}_2\text{H}_6 \) concentration determination is 0.125\%. The response characteristics of low-concentration \( \text{C}_2\text{H}_6 \) gases are determined by reference components with concentration less than 0.125\%, and then, the optimal response function of GC is determined in this concentration range. By the same method, the optimal response function of high-concentration \( \text{C}_2\text{H}_6 \) standard gas samples is determined using the reference component of \( \text{C}_2\text{H}_6 \) concentration greater than or equal to 0.125\%. The gas samples with low-concentration \( \text{C}_2\text{H}_6 \) (6\#, 7\#, 9\#, 10\#, 11\#) are classified as group M, and the gas samples with high-concentration \( \text{C}_2\text{H}_6 \) (1\#, 2\#, 3\#, 4\#, 5\#, 7\#) are classified as group N. Finally, the optimal analysis function is obtained by performing univariate linear regression analysis between the measured value and true value of \( \text{C}_2\text{H}_6 \) in different concentration ranges.

Figure 10 shows the fitting results of the univariate linear regression with different \( \text{C}_2\text{H}_6 \) concentration ranges. When measuring the group M gases, which represent the low-concentration \( \text{C}_2\text{H}_6 \) in the normal period, gas sample 8\# (the \( \text{C}_2\text{H}_6 \) concentration is 0.0898\%) is used as the reference component. When measuring the group N gases, which represent the high-concentration \( \text{C}_2\text{H}_6 \) during the disaster period, gas sample 1\# (the \( \text{C}_2\text{H}_6 \) concentration is 0.186\%) is used as the reference component. On this basis, the univariate linear regression analysis effect between the measured values and the true value is found to be the best. From this, the optimal analysis function of the GC in different \( \text{C}_2\text{H}_6 \) concentration ranges is

\[
y = 1.0927x + 0.000007, \quad x < 0.125\% \\
y = 0.989x + 0.000147, \quad x \geq 0.125\% \tag{8}
\]
4.8. Analysis of C$_2$H$_2$ Measured Results. The key point for the error rate of the C$_2$H$_2$ concentration determination is 0.0463%. The response characteristics of low-concentration C$_2$H$_2$ gases are determined by reference components with concentration less than 0.0463%, and then, the optimal response function of GC is determined in this concentration range. By the same method, the optimal response function of high-concentration C$_2$H$_2$ standard gas samples is determined using the reference component of C$_2$H$_2$ concentration greater than or equal to 0.0463%. The gas samples with low-concentration C$_2$H$_2$ (4#, 6#, 8#, 9#, 11#) are classified as group O, and the gas samples with high-concentration C$_2$H$_2$ (1#, 2#, 3#, 5#, 7#) are classified as group P. Finally, the optimal analysis function is obtained by performing univariate linear regression analysis between the measured value and the true value of C$_2$H$_2$ in different concentration ranges.

Figure 11 shows the fitting results of the univariate linear regression with different C$_2$H$_2$ concentration ranges. When measuring the group O gases, which represent the low-concentration C$_2$H$_2$ in the normal period, gas sample 6# (the C$_2$H$_2$ concentration is 0.0203%) is used as the reference component. When measuring the group P gases, which represent the high-concentration C$_2$H$_2$ during the disaster period, gas sample 1# (the C$_2$H$_2$ concentration is 0.0665%) is used as the reference component. On this basis, the univariate linear regression analysis effect between the measured values and the true value is found to be the best. From this, the optimal analysis function of the GC in different C$_2$H$_2$ concentration ranges is

\[
y = 0.9409x + 0.000006, \quad x < 0.0463\%; \quad y = 1.246x - 0.000066, \quad x \geq 0.0463\% \tag{9}
\]

Meanwhile, the optimal reference component concentration should be selected as follows. (1) During the normal period, H$_2$ is 0.00928%, O$_2$ is 5%, CH$_4$ is 15.1%, CO is 0.497%, CO$_2$ is 0.101%, C$_2$H$_4$ is 0.00998%, C$_2$H$_6$ is 0.0898%, and C$_2$H$_2$ is 0.0203%. (2) During the disaster period, H$_2$ is 4%, O$_2$ is 1.92%, CH$_4$ is 89.9%, CO is 1.84%, CO$_2$ is 22.4%, C$_2$H$_4$ is 0.156%, C$_2$H$_6$ is 0.186%, and C$_2$H$_2$ is 0.0665%.

5. DISCUSSION

Compared with experiments of other studies of mixing gases’ determination, most of them used an internal standard or external standard calibration instrument and correlated the reaction signal with the known gas concentration to accurately quantify the mixed gases via the least-squares method. Velasco-Rozo analyzed the advantages of the internal standard and the external standard for the related experimental setup. To tackle the effect that the concentration and nature of the components of the effluent change over time due to the catalytic reaction, the corresponding mathematical models based on the internal standard and the external standard were established. In addition, Ghasemi established the optimal fitting model for determining the results of multiple mixtures based on multiple linear regression and partial least-squares projections to latent structures, providing a sound theoretical basis. However, currently, there are few studies on the distortion of mixed gases’ measurement results with the GC corrected by the calibration curve. Thus, this paper conducts an in-depth study on this problem. In this paper, 11 groups of mixed gases were determined by calibrated GC. It was found that the error rates of the measured results have a strong correlation with the concentration of the selected reference component and the component to be measured. The key point of each gas is determined by the error scatter diagram, which divides each gas into different concentration groups. Each gas is selected as the reference component to measure the concentration of the corresponding component in other gases with the multiple-point external standard, and the least-squares method is used for linear fitting between measured values and true values. The optimal analysis function is obtained by comparing the regression analysis parameters in different concentration ranges. Calibration of the measured results using these optimal analysis functions is shown in Table 10. It is found that the error rate of measured values corrected by the optimal analysis function is far less than the uncorrected one. It shows the reliability of this method. Therefore, the method not only can alleviate the distortion of the measured results during the disaster period but also can provide powerful environmental monitoring guarantee for mine disaster prevention and rescue work.

6. CONCLUSIONS

To solve the problem of distortion of measurement results by GC, the GC corrected by the calibration curve is used to determine the concentration of 11 groups of mixed gases. It was found that the difference in the error rate of measured results is related to the concentration of the selected reference component and the component to be measured. Every gas is divided into a high- and a low-concentration group by the key points. Compared with the study of the relationship between the reaction signal and the true concentration in mixed gases, the

| serial number | H$_2$    | O$_2$  | CH$_4$ | CO   | CO$_2$ | C$_2$H$_4$ | C$_2$H$_6$ | C$_2$H$_2$ |
|---------------|---------|-------|--------|------|--------|------------|------------|------------|
| 1#            | 0.00429 | 0.065482 | 0.016151 | 0.000367 | 0.012505 | 0           | 0.007176  | 0.004786   |
| 2#            | 0.673538 | 0.016151 | 0.00507  | 0.003732  | 0.011282  | 0.03561   | 0.007296  | 0.021766   |
| 3#            | 0.071385 | 0.000285 | 0.004632 | 0.005251 | 0.018075 | 0.004635  | 0.034804  |            |
| 4#            | 0.161287 | 0.040054 | 0.013045 | 0.006435 | 0.008817 | 0.013837  | 0.011611  | 0.000347   |
| 5#            | 0.030288 |         |         | 0.00265  | 0.009145 | 0.003206  |            |            |
| 6#            | 0.003085 | 0.006277 | 0.021753 | 0.003021 | 0.001634 | 0.000265  | 0.017872  | 0.017542   |
| 7#            | 0.027835 | 0.005974 | 0.015739 | 0.004465 | 0.035465 | 0.019639  | 0.035919  |            |
| 8#            | 0.147319 | 0.014973 | 0.048436 | 0.012077 | 0.045415 | 0.0141    | 0.019989  |            |
| 9#            | 0.003527 | 0.095432 | 0.039489 | 0.001615 | 0.01648  |            |            |            |
| 10#           | 0.153684 | 0.004064 | 0.105818 | 0.064421 |            |            |            |            |
| 11#           |         |        |        |        |        |            |            |            |
multiple-point external standard is used to correlate the measured values and the true values in different concentration groups. Then, the optimal analysis function of each gas can be determined by the least-squares method during the mine disaster period. This method provides a new idea and a practical basis for accurately determining mixed gases. It has far-reaching influence on mine disaster prevention and rescue work. The relevant detailed conclusions are as follows.

(1) Through the experimental results, a large error between the measured result and the true value of the gas concentration was found. The main reason for this is that the concentration difference between the gas to be measured and the reference component is too large.

(2) According to the measurement error rate scatter diagrams of standard multicomponent mixed gases, the key point for distinguishing high and low concentrations is determined by the least-squares method during the mine disaster period. This method provides a new idea and a practical basis for accurately determining mixed gases.

(3) Every standard multicomponent mixed gases is divided into high and low concentration groups by the key points; the high- and low-concentration gases are selected as the reference components to fit univariate linear regression analysis between the measured results and the true values of gases in the corresponding concentration range. Comparing the $r^2$ and $SS_{oo}$, the optimal analysis function and the reference component concentration in different concentration ranges can be determined.

(4) Through calibration of measured results using these optimal analysis functions, it is found that the error rate between the calibration result and the true value is much less than the result without calibration. This proves the reliability and superiority of the method, and the method can provide strong support for mine disaster prevention, hazard identification, and rescue work.

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Notes
The authors declare no competing financial interest. All data included in this study are available upon request by contact with the corresponding author.

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