



Article Effect of Secondary Oxidation of Pre-Oxidized Coal on Early Warning Value for Spontaneous Combustion of Coal

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Abstract: The indicative ability of a gas indicator for the spontaneous combustion of coal is affected by the secondary oxidation of oxidized coal, from old goafs, entering a new goaf through air leakages. This phenomenon can affect the accuracy of early warning systems regarding the spontaneous combustion of coal in a goaf. In this research, three kinds of coal were selected to carry out a spontaneous combustion simulation experiment in which a temperature-programmed experimental device was used to analyze the behavior of the index gas towards raw coal and oxidized coal, for which the latter was oxidized at 70 °C, 90 °C, 130 °C, and 150 °C. The results show that the chain alkane ratio in the secondary oxidation process and the trends of oxygen, CO, and C_2H_4 concentrations are the same as those in the primary oxidation process. On the other hand, the temperature at which C_2H_4 initially appears, during secondary oxidation, is lower than in primary oxidation. The CO produced in the early stage of secondary oxidation is greater than the CO produced, at the same temperature, in primary oxidation. In this regard, the usage of C_2H_4 concentration as an indicator with which to judge the occurrence of the spontaneous combustion of coal would allow for an earlier response. In the secondary oxidation process, the temperature of the extreme value of the alkene ratio appears higher than in primary oxidation. The presence of a higher pre-oxidation temperature and a higher proportion of secondary oxidation gas will affect an indicator's judgement when the primary oxidation enters the severe oxidation stage. The gas produced by secondary oxidation will affect the early warning of the spontaneous combustion of coal in the coal mine goaf, which should be considered in the establishment of an early warning system.

Keywords: coal; spontaneous combustion; secondary oxidation; gas index; fire warning

1. Introduction

The spontaneous combustion of coal is one of the most important causative factors of mine fires, which can produce a large amount of toxic and harmful gases, threatening the health and safety of workers, and even causing disasters such as explosions [1–3]. When coal is exposed to air soon after the mining process, it starts to react with oxygen to generate heat; subsequently, there is an accumulation of heat that can cause the spontaneous combustion of coal [4]. In some cases, the heating conditions of coal oxidation will be severely altered, thereby interrupting the heating process and causing the coal temperature to begin to reduce to ambient temperature, which, in turn, leads to the formation of oxidized coal. The process of the oxidation and heating of the already oxidized coal that is exposed to air again is defined as secondary oxidation, which is a common behavior in underground mining, e.g., in a mine with a composite coal seam where an air leakage channel is formed due to the collapse-related disturbance of the goaf when the lower coal seam is mined.



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Once fresh air enters the old upper goaf, the oxidized residual coal is exposed to oxygen again, and secondary oxidation will occur [5], which is why it is one of the most significant causes of internal coal mine fires.

Compared with primary coal oxidation, the reaction characteristics of the secondary oxidation of oxidized coal are more complex to define [6,7]. Tang et al. [8] found that secondary oxidation causes changes in the microstructure of lignite and increases the risk of the spontaneous combustion of lignite. However, excessive pre-oxidation will consume organic components, which reduces the propensity for self-heating.

Xu et al. [9,10] studied the changes that occurred in free radicals in the secondary oxidation process via Electron paramagnetic resonance (EPR) spectrometer. In addition, they described the behavior of free radicals in the secondary oxidation process, finding that secondary oxidation has a greater effect on the reactivity of high-rank coal. Wang et al. [11] investigated the influence of the degree of oxidation and ventilation flow rate on the spontaneous combustion of coal through six sets of programmed temperature experiments, concluding that primary oxidation promotes the early stage, but it has an inhibitory effect in the later stages of spontaneous combustion. Pis et al. [12] carried out experiments to simulate the entire process of the spontaneous combustion of six oxidized coal samples using a thermal analyzer, finding that the critical temperature point of each coal sample showed a different degree of increase with the increase in the oxidation degree, while the ignition point temperature showed a decrease. Worasuwannarak et al. [13] carried out spontaneous combustion experiments on different oxidized coal samples via TGA-MS and concluded that the coal samples produced more CO and CO₂ with the increase in the oxidation degree. Thus, Wang et al. [14–16] pointed out that the pre-oxidation temperature is a key factor that affects the secondary oxidation of coal, and that preoxidation increases the activation energy of coal in the endothermic stage. Pre-oxidation below 110 °C inhibits the spontaneous combustion of coal, while pre-oxidation above 130 °C confers a promotional effect. Zhang et al. [17] found that nitrogen can inhibit the generation of oxygen-containing functional groups and the decomposition of aliphatic hydrocarbons during secondary oxidation. In this regard, as coal mining productivity increases, secondary oxidation occurs more frequently and, often, simultaneously with primary oxidation.

At present, there are many early warning methods for the spontaneous combustion of coal [18,19], with the characteristic gas index being the most common and effective method [20]. Chen et al. [21] used CO and C_2H_4 as the main indicators and C_2H_6 and C_2H_4/C_2H_6 as auxiliary indicators to divide the stages of spontaneous combustion. Lu et al. [22] pointed out that C_2H_6 and temperature have poor regularity, with the appearance of C_3H_8 at high temperatures, and neither of them are suitable gas warning indicators in the low-temperature stage of spontaneous combustion. Niu et al. [23] eliminated the error caused by the different initial concentrations of the index gas at different locations by introducing the K value. Zhang et al. [24] divided the spontaneous combustion of coal into seven stages, using six characteristic temperatures, and provided the gas index and threshold values corresponding to each characteristic temperature. Based on the original analysis of indicator gas concentrations and ratios, Deng et al. [25] introduced the growth rate of the indicator gas to optimize predictors.

The above research reveals the law and mechanism of the primary oxidation and secondary oxidation of coal with respect to its spontaneous combustion, as well as a variety of gas warning indexes and systems. Moreover, it is well known that old goafs often have gas exchanges with new goafs [26–29]. The gases produced in the secondary oxidation process are the same type as those produced in primary oxidation, which will affect the concentration of the original gas field in the mining area and result in a judgment deviation of the severity of the spontaneous combustion of coal in the goaf from the coal seam in question. Currently, the early warning indicators and critical values of the spontaneous combustion of coal are generally determined by collecting fresh coal samples at the working face and then carrying out temperature-programming experiments in a laboratory, which

are used to guide the work regarding the development of an early warning system for the spontaneous combustion of coal at a coal mine site. This has important guiding significance for warning systems for the spontaneous combustion of coal and oxidation in separate goaf that have not been connected with an old goaf [30,31]. However, whether the gas produced by the secondary oxidation of the old goaf will affect the corresponding relationship between the early warning value and the temperature of the goaf being mined still requires further research to be determined.

In this study, secondary oxidation experiments of oxidized coal from three coal mines were carried out using a coal oxidation and temperature rise experimental system. Thus, the gas generation law and its corresponding relationship with temperature are analyzed herein. The influence of the second oxidized gas entering the goaf on the gas early warning index is discussed, while the existing gas early warning index is optimized and corrected. Ultimately, this study provides new ideas to be applied in early warning systems for the spontaneous combustion of coal gas and for the improvement of the accuracy of early warning systems and the scope of their application so as to guide the effective prevention and control of the spontaneous combustion of coal in underground coal mining.

2. Materials and Methods

2.1. Coal Samples

Coal samples used in the study were collected from several Chinese provinces, namely, Guizhou, Liaoning, and Shanxi, and the samples were denoted as GZ, LN, and SX, respectively. Coal samples were taken from the working face, immediately stored in a closed coal sample tank, transported to the laboratory, and kept in nitrogen. The analytical results regarding the three coal types are shown in Table 1.

Table 1. Samples' analytical results.

| | M _{ad} (%) | A _{ad} (%) | V _{ad} (%) | FC _{ad} (%) |
|----|---------------------|---------------------|---------------------|----------------------|
| GZ | 3.30 | 9.89 | 6.60 | 80.21 |
| LN | 3.55 | 20.63 | 32.65 | 41.37 |
| SX | 1.22 | 19.835 | 13.98 | 64.96 |

2.2. Experimental Apparatus

As shown in Figure 1, the coal oxidation and temperature rise experimental system is mainly composed of a gas supply device, a temperature-programming system, a gas chromatograph, and a control terminal. The gas supply provides continuous and stable gas for the temperature-programmed device, ensuring a relatively stable gas environment during the temperature-programming process. There is a sample reactor inside the temperature programming system, with two temperature sensors to monitor the internal and external temperatures of the sample reactor. The temperature-programmed device can continuously increase the internal temperature from 0 °C to 200 °C, with a minimum heating rate of 0.2 °C/min. The outlet pipeline of the sample reactor is connected to the gas chromatograph through the condenser. The gas chromatograph is used to analyze the content of various gases produced by coal oxidation during the heating stage. Moreover, the control terminal can manage heating parameters and record temperature data.



Figure 1. Coal oxidation and temperature rise experimental system.

2.3. Experimental Process

LN coal samples were crushed and segregated into five particle-size ranges: 0.280-0.224 mm, 0.224-0.180 mm, 0.180-0.125 mm, 0.125-0.074 mm, and 0.074-0 mm. Consequently, five coal samples with an equivalent weight of 40 g were obtained using a mixture of 10g from each particle-size range. The five coal samples were dried at 40 °C in a vacuum-drying oven for 48 h to remove moisture. Then, the coal samples were placed into the sample reactor of the temperature-programming device. The temperature rise rate was set at 0.5 °C/min, and 40 mL/min of dry air was delivered to the sample reactor by the gas supply device. Different coal samples were heated from 30 °C to 70 °C, 90 °C, 130 °C, and 150 °C. After reaching the preset temperature, the samples were kept in the sample reactor for 30 additional minutes. Subsequently, the gas supply device was adjusted to transport nitrogen at the same flow conditions, and the coal samples were naturally cooled to room temperature in a nitrogen environment. Four coal samples were oxidized coal samples, which were denoted as LN-70, LN-90, LN-130, and LN-150; the remaining untreated coal sample was denoted as LN-raw.

The device was again set to transport dry air at 40 mL/min to oxidize the coal samples (LN-70, LN-90, LN-130, LN-150, and LN-raw) from 30 $^{\circ}$ C to 170 $^{\circ}$ C at a heating rate of 0.5 $^{\circ}$ C/min. In this process, the gas concentration at the outlet was detected every 20 min by a gas chromatograph.

The same procedure was performed for the other two coals (GZ and SX), for which a similar nomenclature was followed as that for the different coal samples (GZ-70/SX-70.....).

3. Results and Discussion

3.1. Spontaneous Combustion Stage Division and Index Selection

This section uses the LN samples as an example to select the indicator gases and divide the spontaneous combustion of coal stages while considering the existing research [24]. As shown in Figure 2, the process of the spontaneous combustion of coal is divided into six stages.

- Stage I: oxidation stage (t < 50 °C). At this stage, coal begins to slowly oxidize, and every forecast indicator rises slowly. This stage can be characterized by the CO concentration, which is less than 17.225 ppm, and the spontaneous combustion of coal.
- Stage II: self-heating stage (50 °C < t < 0 °C). At this stage, the increase in CO/O₂ is accelerated, and the reaction rate of coal and oxygen is slowly increased. The accumulated heat can increase the temperature of coal.
- Stage III: accelerating stage (70 °C < t < 90 °C). The main indication that this stage has been entered is the appearance of C_2H_4 , which indicates that coal oxidation is beginning to accelerate, and the rapid increase in C_2H_6 and CO/O_2 . After this stage begins, the spontaneous combustion of coal will be difficult to control.

- Stage IV: intense stage (90 °C < t < 120 °C). The indication that this stage has begun
 is the presence of C₂H₆/CH₄ at its maximum value. At this time, the coal sample
 reaction is intense, and C₂H₄ begins to increase rapidly.
- Stage V: pyrolysis stage (120 °C < t < 160 °C). This stage is marked by the maximum amount of C_2H_4/C_2H_6 , followed by a slower rate of increase.
- Stage VI: fission stage (t > 160 °C). At this stage, the formation rate of C₂H₄ is lower than C₂H₆, while the maximum C₂H₄/C₂H₆ value appears.



Figure 2. The division of the stages of the spontaneous combustion of coal.

3.2. Oxygen Concentration

Although oxygen concentration cannot be directly used as an indicator of the spontaneous combustion of coal, it is an important indicator in this process, since the series of chemical reactions that occur during this process are related to oxygen consumption [32]. In this experiment, dry air flowed in from the bottom of the sample reactor, passed through the coal chamber, and then flowed out from the top of the sample reactor, while the gas components were analyzed at the outlet by gas chromatography. Figure 3 shows the oxygen concentration of the different coal types during the temperature-programmed process. Figure 3 shows how the oxygen concentration gradually decreases as the temperature increases. Under the same conditions, LN (low-rank coal) consumes the most oxygen and GZ consumes the least. This is due to the high content of oxygen-containing active functional groups in low-rank coal, which are more easily oxidized, consuming more oxygen under the same conditions. The oxygen-containing active functional groups of anthracite are gradually reduced after metamorphism, so the degree of oxygen consumption is less. LN has little change in terms of its oxygen content until 80 °C, after which it decreases rapidly. The oxygen concentration of the GZ coal and the SX coal drops rapidly at 110 °C and 100 °C, respectively. This is also related to the metamorphic degree of coal. The oxygen concentration in the second oxidation process changes compared with the oxidation process of raw coal, but the behavior is similar. The oxygen concentration of SX-70 is lower than SX-raw because pre-oxidation causes the water to evaporate in the coal, which causes the reaction rate and the degree of oxygen consumption to increase [33]. The oxygen concentration of the other coal types in the secondary oxidation process at the same temperature is higher than that during primary oxidation. This is because a large number of active functional groups, which are easily reactive, are consumed during the pre-oxidation process. Therefore, oxidized coal does not react as easily with oxygen compared to raw coal, resulting in a reduction in oxygen consumption.



Figure 3. Oxygen concentration at the outlet of different coals during temperature programming: (a) GZ; (b) LN; (c) SX.

3.3. Oxidation Gas Products and Ratios

Coal has a complex chemical reaction with oxygen during spontaneous combustion, CO and CO₂ are the main oxidation gas products. Both gases have a good linear relationship with temperature. However, there is a CO₂ reserve in a coal seam, and the breathing of workers also produces CO₂, resulting in a non-unique source of CO₂. Therefore, CO₂ has not been selected as the only indicator gas, given that CO has a single source that can be used as a gas indicator [34]. CO/ Δ O₂ was selected as an auxiliary index that can avoid the influence of air volume on gas concentration [35].

CO is widely used as an indicator gas in coal mines in China. It can be seen from Figure 4 that all curves show the same behavior. The CO concentration increased slowly at the initial stage and then began to rise rapidly. In the early stage of coal oxidation, the CO produced by oxidized coal is greater than in raw coal. This is because the raw coal contains a high level of moisture, which will evaporate and absorb heat in the early stage of the spontaneous combustion of coal, thereby reducing the reaction rate of coal and oxygen, and thus the raw coal produces less CO. On the one hand, the evaporation of water increases the pore and specific surface area of coal, which increases the contact area between coal and oxygen, so more CO is produced in the secondary oxidation process. After 100 °C, the free water evaporates completely, and the raw coal also has larger pores and a greater specific surface area, so the coal oxygen reaction intensifies, along with the level of CO. Moreover, the CO-producing groups in the coal are not overconsumed because the raw coal is not pre-oxidized, making the amount of CO produced by raw coal greater than that produced by the pre-oxidized coal. This behavior is similar to the oxygen change law. CO is often used as a forecast gas for the early stage of coal oxidation. For LN, when the CO concentration is lower than 17.225 ppm, it is considered to be in the oxidation stage, but in the secondary oxidation process, when the temperature reaches 40 $^{\circ}$ C, the CO concentration exceeded 17.225 ppm; therefore, the mixing of secondary oxidation gases can cause the CO concentration to appear greater than the actual amount present, causing the forecast stage to occur after the fact.

Figure 5 shows the variation of $CO/\Delta O_2$ during the programmed temperature rise for the different coal types. It can be seen from Figure 5 that the increase in the $CO/\Delta O_2$ ratio of the oxidized coal, during the secondary oxidation process, occurs linearly with temperature, like the raw coal sample. In the low-temperature oxidation stage (30–80 °C), the $CO/\Delta O_2$ ratio of oxidized coal rises very slowly, but the value is significantly higher than raw coal.



Figure 4. CO concentration at the outlet of the sample reactor: (a) GZ; (b) LN; (c) SX.



Figure 5. $CO/\Delta O_2$ behaviors of different coal types: (a) GZ; (b) LN; (c) SX.

On the one hand, the decrease in moisture grants the pre-oxidized coal a larger specific surface area, thereby increasing the production rate of CO and the consumption rate of O_2 . On the other hand, pre-oxidation causes some functional groups in coal to react with oxygen to form intermediate products, so less O_2 is needed in the early stage of the secondary oxidation process to generate more CO. In the case of the GZ samples, the difference between the CO/ ΔO_2 ratio of oxidized coal and raw coal after 80 °C is not significant. For LN-90 and LN-150, in the secondary oxidation process, the CO/ ΔO_2 ratio is significantly less than in raw coal after 100 °C. The GZ coal samples also have a large difference in CO/ ΔO_2 values between raw coal and oxidized coal after 100 °C. The CO/ ΔO_2 value is often used to predict the coal temperature and spontaneous combustion degree in goafs because of its good linear relationship with temperature. However, the participation of secondary oxidation gases can lead to errors in temperature determination, especially for low-rank coals after 100 °C.

3.4. Pyrolysis Gas and Ratio

Pyrolysis gasses are alkanes, olefins, and alkynes produced by the decomposition of organic components during the spontaneous combustion of coal, mainly including CH₄, C_2H_6 , C_3H_8 , C_2H_4 , and C_2H_2 . CH₄ and C_2H_6 are native endogenous gases in coal seams and are usually not selected as indicator gases alone. The presence of C_2H_2 indicates that coal is in the combustion stage, so it is usually not selected as an indicator gas in the low-temperature oxidation stage [36]. The appearance of C_2H_4 indicates that the spontaneous combustion of coal has entered the accelerated reaction stage, so C_2H_4 is an important indicator gas [37]. The alkane ratio and olefin–alkyl ratio can effectively eliminate the influence of wind flow on the indicator gas and has a good linear relationship with temperature [38]. Therefore, C_2H_4 , the alkane ratio, and the olefin–alkyl ratio were selected as gas indicators for analysis in this section.

Figure 6 shows the same behavior of C_2H_4 production for the different coal samples during the programmed temperature rise. C_2H_4 is not detected at 30 °C, indicating that C_2H_4 is not a gas that is originally present in these three types of coals. With the increase in temperature, C_2H_4 began to appear, first with slow growth and then rapidly. The C_2H_4 occurrence temperature of the oxidized coal was lower than in the raw coal, and the occurrence temperature of C_2H_4 decreased with the pre-oxidation temperature increase. This means that oxidation causes the coal to enter the accelerated oxidation stage much earlier. For the LN and SX coal samples, at the later stages of oxidation, the amount of C_2H_4 produced by the raw coal is greater than that produced by the pre-oxidized coal. Pre-oxidation will reduce the activation energy of the reaction and form some intermediate products. Therefore, C_2H_4 can be produced at a lower temperature during the secondary oxidation process. Since high-temperature pre-oxidation. Once the gas generated by secondary oxidation enters the goaf, the use of the time when C_2H_4 occurs to determine the beginning of the accelerating stage will yield a time earlier than of the actual situation.



Figure 6. C_2H_4 concentration at the outlet of the coal sample reactor: (a) GZ; (b) LN; (c) SX.

The alkane ratio is the concentration of alkane to the concentration of methane or ethane. Extreme values or abrupt increases in the alkane ratio during oxidation are a sign that the oxidation process has reached an intense stage. C_2H_6/CH_4 was selected as the index in this section.

As can be seen from Figure 7, the LN and GZ coal samples increased first and then decreased with the temperature increase. Whereas SX increased first, and then decreased and increased again. The alkane chain ratio value in the secondary oxidation process is lower than in primary oxidation. The peak of the chain alkane ratio during the secondary oxidation of oxidized coal occurs at a higher temperature than in raw coal, especially after high-temperature oxidation. The GZ-raw coal's maximum value occurs at 90 °C, while the extremes value of GZ-150 occurs at 130 °C. LN-150's maximum value occurs 20 °C higher than in raw coal. Following a similar pattern, the difference between SX-raw and SX-150 is 10 °C.

Scholars often regard the point of the occurrence of the extreme value of the chain alkane ratio as the beginning of the intense oxidation of coal. Therefore, a certain percentage of secondary oxidation gas is simulated as being mixed into the primary oxidation gas to verify if there is an effect on the occurrence temperature of the extreme value. LN was taken as an example, for which different proportions of raw coal oxidation gas were mixed with secondary oxidation gas to calculate the extreme value of the alkane ratio. Figure 8 shows how the degree of influence is closely related to the oxidation temperature and the mixing ratio. At low oxidation temperatures, the difference in the chain alkane ratio between primary and secondary oxidation is small; therefore, the mixture of gases does not affect the occurrence time of the extreme value will only be affected when the secondary oxidation gas occupies a larger proportion. Therefore, the gas produced by secondary oxidation will



affect the determination of the alkane ratio when it is related to the oxidation temperature and the participation ratio of the secondary oxidation gas.

Figure 7. Alkane ratio during temperature programming: (a) GZ; (b) LN; (c) SX.



Figure 8. The temperature at which the extreme value of the alkane ratio appears.

The olefin-alkane ratio refers to the ratio of the presence of a long-chain olefin to methane or ethane. In this study, the C_2H_4/C_2H_6 ratio was selected for analysis. It has strong regularity during temperature change, and it is often used as an auxiliary index to predict the spontaneous combustion of coal. Figure 9 shows that the C_2H_4/C_2H_6 ratio increases with temperature. However, the olefin-alkane ratio and temperature are not linear in the secondary oxidation process of oxidized coal. The oxidized coal types show an increasing and then decreasing peak-like curve at low temperatures during secondary oxidation, where the peak becomes more obvious as the oxidation temperature increases. The temperature corresponding to the first appearance of C_2H_4/C_2H_6 is also different from the primary oxidation one, which is due to the different C_2H_4 occurrence times. The occurrence temperature behavior is the same as that of C_2H_4 . The extreme value (inflection point) of C_2H_4/C_2H_6 can be used as a sign that the coal-oxygen reaction has entered the fission stage. At this time, C_2H_4 and C_2H_6 are produced in large quantities, but C_2H_4 has a high formation rate, so the olefin ratio begins to decrease. In the case of the GZ samples, the minimum value did not appear at 170 °C, so it was impossible to judge whether the gas produced by secondary oxidation would affect the determination of the fission time, while the coal type at a higher temperature oxidation temperature made this point advance in time. The mixing of secondary oxidation gas will have an impact on its accuracy. However, the temperature in the fission stage is generally high (140–180 $^{\circ}$ C). At this time, spontaneous combustion is generally difficult to control. Therefore, it is less useful for early warning systems for fire, but it is still useful as an indicator for judging the degree of the spontaneous combustion of coal.



Figure 9. Olefin–alkane ratio during temperature programming: (a) GZ; (b) LN; (c) SX.

4. Conclusions

This paper used a coal oxidation and temperature rise experimental system to conduct primary oxidation experiments and secondary oxidation experiments on coal types with different metamorphic degrees. The influence of the secondary oxidation gas on the early warning indicator gas in the primary oxidation process of coal was studied, and the gas products in the oxidation process were analyzed. Overall, the following conclusions were obtained.

(1) In the coal oxidation stage, the CO concentration produced by the secondary oxidation of oxidized coal is higher than in raw coal. The mixing of secondary oxidation gas makes the CO concentrations appear higher than the actual value, thus influencing the judgment of the stage of the spontaneous combustion of coal, which would be later than the actual situation.

(2) In oxidized coal, the initial appearance time of ethylene in the secondary oxidation process occurs earlier. With the participation of a secondary oxidation gas, when using C_2H_4 as an indicator to judge the time at which coal enters the rapid oxidation stage, the result would be earlier than the actual situation.

(3) Pre-oxidized coal enters the intense oxidation stage later than raw coal. The high pre-oxidation temperature and the large proportion of secondary oxidation gas affect the occurrence time of the extreme value of the chain alkane ratio in raw coal so that the judgment of this point at the intense oxidation stage occurs later than that in raw coal.

(4) The gas produced by secondary oxidation interferes with the early warning of the spontaneous combustion of coal when using an index gas. In a real situation, the secondary oxidation of coal may occur, for which it is necessary to select the correct index value.

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