Methods to determine the status of mine atmospheres - an overview

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Abstract

On a regular basis, mine personnel should obtain air samples directly from active underground areas as well as remotely from sealed locations. These samples provide mine officials with data relative to the makeup of the various atmospheres. Should conditions underground change, these results can provide a baseline that can assist officials in determining the extent of change. Relating the concentrations of individual gases to time, applying gases to equations, and examining their change-over time are tools that have been successfully used to determine if a heating event exists and, if so, the extent of the emergency. These atmospheric status equations have either been developed for the mining industry or adapted from other industries. They serve as tools to assist personnel in determining the condition of underground mine atmospheres. As long as the problem area continues to be ventilated, certain gases, gas ratios, and equations can be used to determine if a fire exists, what type of material could be burning, and what quantity of coal is burning. Once the mine or the involved section has been temporarily sealed, gases, ratios, and gas-derived equations can assist personnel in determining how conditions within the sealed volume are changing over time. To alleviate potential explosions when fresh air is once again introduced into the sealed volume, equations and a diagram have been developed to predict the likelihood of an explosive atmosphere. Similarly, prior to commencing recovery of a mine or section, equations exist that can assist in determining if the fire will rekindle when air is reintroduced. This paper serves as an overview to remind and/or instruct readers about gas-sampling methodologies and gas analyses to assist in determining the status of underground atmospheres.

Introduction

Obtaining atmospheric samples on a regular basis during normal operations establishes a reliable baseline. Based on these numbers, a mine operator can effectively determine if the atmosphere has changed. In the event of a fire-related emergency, gas samples become critical to those persons delegated to fighting the fire. These samples can provide rescue persons with vital information on the status of the atmosphere (Koenning, 1987).

It is important to understand that individual sample results often mean little. It is typically more important to follow the trends that multiple samples produce. This does not mean that individual samples should be ignored. At times, especially when the atmosphere is relatively static, an individual sample can indicate a change in activity. Again, however, when a change is detected, the sampling frequency should be increased so that adequate backup data are obtained.

Mine personnel should understand what type of fire is likely and how this potential source could influence the spread of fire. For example, if the mine is prone to spontaneous combustion or rapid oxidation, tests for coal gases such as carbon monoxide (CO), carbon dioxide (CO_2), and hydrogen (H_2) should be performed. Coal samples can be extracted and examined in a laboratory capable of simulating different stages of heating. From these tests, gas samples can be obtained for the different heating phases.

Faced with a fire, mine officials, responsible for the safety of miners and mine rescue personnel, must make difficult and potentially life-threatening decisions. Almost immediately, one must decide if conditions are suitable for fighting the fire directly, or if the affected area should be sealed and the fire fought indirectly. The difficulty increases if miners are trapped or missing.

Preparation should be made for just such an occurrence. This article has been written to instruct readers about methods available to assist in determining the status of the mine atmosphere. Specific pieces of hardware, such as gas sample containers, manometers, sample pumps, flexible tubing, handheld gas detectors, and a recording barometer should be on hand.

Sampling Techniques

There are two methods for obtaining gas samples. Real-time instruments are designed to provide nearly instanta-

neous results. They range from hand-held sample tubes to more complex, larger, and less portable instruments. A number of different technologies perform real-time gas analyses. These include stain-tube chemical sensors, electro-chemical reactions, and infrared sensors.

The second technique for analysing sampled gases is the gas chromatograph (GC). These instruments are typically housed in a transportable laboratory or a building. Unlike real-time instruments, the period required for analysis results in a time interval between sample acquisition and analysis results. The GC is often used to compare results obtained with real-time samplers. This is especially true when interfering gases and high background gas levels (such as carbon dioxide background when using infrared instruments) are present. Instantaneous and GC results should be compared on a regular basis. McNider (1985) provides a description of the importance of having a gas chromatograph available as well as obtaining gas samples on a regular basis.

There are two GC types, each based on gas concentration. The flame ionisation detector-type gas chromatograph is used for low gas concentrations. It is very sensitive and can detect a large range of concentrations; however, this analytical method destroys the gas sample. The thermal conductivity detector-type gas chromatograph is used when gas concentrations are high. It is less sensitive, but it does not destroy the sample. Gas chromatography samples are normally obtained either by pulling a sample into a container that has been air-evacuated or by forcing the sample into a container through an air pump.

A container often used by NIOSH personnel is the 10-to-20 ml air-evacuated glass sampling tube. These are blood collection tubes that have been at least 95 air evacuated (Timko, 1991). Unfortunately, as they age, small quantities of CO have been detected in these tubes. Freedman et al. (1975) have reported that tube storage should not exceed one-to-two months when analysing low levels of CO.

The Mine Safety and Health Administration (MSHA) prefers syringes that can be cleaned and reused. Many operators use Mylar bags of varying volumes to sample gases.

The easiest way to visualise the status of the atmosphere is to graph the collected data. Most gas concentrations and formulae presented in this work are commonly graphed in a semi-logarithmic format. This format is used when the data cover a very wide range or when one desires to transform a complex function into a linear function. An exception to the semi-log format is the Explosibility diagram (Figure 3). In addition, Francart (2005) has reported that, in many instances, linear plots are just as effective in determining the status of the atmosphere.

When analysing for fire, one must obtain gas samples at the same locations at specific and frequent time intervals. Handheld and gas chromatography samples should be taken at the main fans and key air splits. If possible, sampling lines should be installed into return airways or areas that may become inaccessible. A simple, clear, color-coded mine map containing key air split readings should be generated. Estimate where the fire is located.

Track gas liberation rates using concentrations and ventilation readings. Many times only concentrations are examined. Since conditions often change relative to varying air quantities, looking at both gas concentration and ventilation will generate a more accurate determination of actual gas levels.

Once the decision is made to seal the area or the entire mine, additional rules of thumb apply. Adequate remote gas sampling locations must be established. Sample lines should be extended into the entry by the proposed seal location. In addition, remember to install larger pipes in the seal for possible water or inert gas injection.

When obtaining a gas chromatography sample, it is important to determine that the sample line is out-gassing before taking a sample. This reduces the likelihood that atmospheric gases will enter the sample and dilute the result. Ensure sample accuracy by thoroughly purging the tubing before obtaining a sample. If a significant quantity of methane is being liberated, have 0-to-100 methane detection instruments available.

Sampling should be performed at regular around-the-clock intervals to ensure that diurnal pressure changes are not affecting the results. One must be especially careful in analysing sample results whenever a steep atmospheric pressure gradient, caused by a strong cold front or deep low-pressure system, is affecting the area. A sealed mine typically has a regular diurnal pattern, based on daily temperature fluctuations (Francart, 1997). Government and private weather forecasting sources are available to predict barometric pressures. One should never take gas samples when the ambient or outside barometric pressure is higher than the pressure within a sealed area. This imbalance can cause air to in-gas or flow into the sealed volume which raises problems because the potential for sample dilution is high. Table 1 shows gas samples taken from behind a seal in a main return. This purpose of this table is to show that, even at a location where out-gassing is most common, dilution can still occur.

Table . Out-gas vs. n-gas Sampling

Sample	Oxygen	Nitrogen	Carbon Dioxide	Methane
Out-gas	0.5	38.2	14.0	45.0
In-gas	18.5	74.0	2.1	4.4

Be wary of large changes in individual gas samples. Although pressure changes across seals can be instantaneous, equalising gas exchange takes time. The pressure within the entire sealed volume must equalise with the outby atmosphere before the potential for gas exchange across the seals stops.

Gases

For this work the gases are divided into two general categories: atmospheric gases and by-products of oxidation or combustion. Atmospheric gases are those typically found in an ambient gas sample and include nitrogen, argon, oxygen, and carbon dioxide. Oxidation, or combustion byproducts, consist of carbon monoxide, hydrogen, and the alkane (C_NH_{2N+2}), alkene (C_NH_{2N}), and alkyne (C_NH_{2N-2}) series of hydrocarbon gases.

The progression of evolving gases is dependent on the temperature of oxidation. Typically, carbon dioxide is emit-

ted first, followed by carbon monoxide and hydrogen. As temperatures increase, flaming combustion often occurs just after hydrogen is detected. Finally, hydrocarbons such as ethylene and propylene are routinely detected following the initiation of fire.

The configuration of the GC determines how many different gases are able to be analysed. Some GCs are capable of analyzing a large number of gases. Because of number rounding and limited resolution of very low gas concentrations, the sums of these analysed gases may not equal exactly 100 . When using less capable GCs, certain gases are not analysed. In this instance, all analyzed gases are summed and this value is subtracted from 100 . The remainder is the concentration of all gases not analysed. This mathematical process is called gas normalising.

Nitrogen

Nitrogen gas (N_2) is the most abundant gas, comprising 79 of the ambient atmosphere. N_2 is inert; the number of moles of gas will remain the same even when the gas passes through an area undergoing combustion. Nitrogen gas density is 0.9671, compared to dry air. Analyses normally involve adding argon gas (Ar) to N_2 values[2]. Several equations dealing with fire existence, fuel, status, and potential explosibility require that N_2 values be measured, rather than normalised.

Blackdamp is a hazardous, low oxygen phenomenon that occurs in poorly ventilated areas. Since nitrogen makes up the greatest proportion of atmospheric gases, an atmosphere in which oxygen has been consumed will be composed of mainly nitrogen. In sealed underground oxygen-depleted atmospheres, the production of carbon dioxide will also result in blackdamp.

Oxygen

In a normal atmosphere, oxygen gas (O_2) comprises slightly less than 21 by volume. Its density is 1.105 relative to dry air. The minimum O_2 concentration allowed where miners normally work or travel in a coal mine is 19.5 (30 CFR, 75.321 (a)(1)). Oxygen is typically not considered a contaminant. As it passes through a mine, its concentration becomes less because of oxidation, including fire, with underground components. If a sufficient quantity of O_2 is consumed, the atmosphere becomes oxygen deficient, represented by $)O_2$. This deficiency can be calculated by:

$$)O_2 \quad 0.265N_2 - O_2$$

where:

$)O_2$ oxygen deficiency,

N_2 measured nitrogen,

O_2 measured oxygen,

0.265 ratio of ambient oxygen to nitrogen

Mitchell (1990) stated that this calculation is valid only when air is flowing into the fire area and the O_2-to-N_2 ratio of this air is 0.265. If $)O_2$ is increasing, the fire is consuming more fuel. Conversely, low $)O_2$ typically signifies ambient conditions or low-level reactions taking place.

[2] In this paper, all N_2 values imply N_2 + Ar

Table 2. Examples of Oxygen Deficiency

Sample	O_2	N_2	$)O_2$
1	20.94	79.02	0.00
2	10.67	80.16	10.57
3	20.62	79.06	0.33

Sample 1 in Table 2 shows a ventilated entry under ambient conditions. In Sample 2, an active airway fire existed. Finally, Sample 3 was obtained under the same conditions as Sample 2; however, the results were diluted by other air splits. A thorough understanding of variables associated with specific sampling locations is required.

Carbon Dioxide

Carbon dioxide (CO_2) is considered a primary fire detection gas. Because its density (1.519) exceeds that of air by more than 50 , in low ventilation velocities it will most likely be found near the floor. The maximum time-weighted average permitted in bleeder entries traveled by miners is 0.5 and the short-term exposure limit is 3 (30 CFR, 75.321 (a)(1)).

Carbon dioxide is a gas formed in a variety of ways. It is a major product of combustion. Normally, it is liberated by micro-organisms oxididing coal or by mixing acidic mine water with calcium carbonate, found either in surrounding strata or in rock dust. Gas samples can contain more CO_2 than is actually being generated by combustion. On the other hand, CO_2 is soluble in water; therefore, samples may contain less CO_2 than is actually being evolved. Some mines liberate CO_2 similarly to methane. It is important to determine, in advance, if this is occurring so that its influence on the fire equations is known.

Carbon dioxide is produced abundantly in fires. In these situations, its concentration will most likely be greater than other gases. Mitchell (1990) states that there are three methods to assist in determining that increasing CO_2 levels are fire-related:

1. The trend of N_2 is relatively flat,
2. Where the CO_2 trend rises, the O_2 trend should decrease at the same or a greater rate, and
3. The sum of $CO_2 + CO + H_2$ (in percent) is less than the $)O_2$, again in percent.

While CO_2 is an important indicator, other atmospheric and fire-related gases should simultaneously be examined. If an inert gas, such as CO_2 or N_2, is injected into a sealed area, the effects of this effort on the entire sealed atmosphere must be considered. Table 3 provides results of inerting a longwall gob atmosphere following an active fire within the gob. If 37 CO_2 by volume was injected into the fire, the resulting N_2 and O_2 concentrations should have been approximately 50 and 13 , respectively. Obviously the fire had some effect on the outcome.

Table 3. Sealed Longwall panel before and after CO_2 in ection

	O_2	N_2	CO_2
Before	19.80	79.73	0.87
After	1.27	57.46	38.09

Carbon Monoxide

Carbon monoxide (CO) is used as a fire detection gas more frequently than any other gas. Its density is only slightly less than dry air (0.97 versus 1.00), so it will readily diffuse with surrounding gases. McPherson (1993) explains that, when heated, CO can be found with smoke in layers along the roof.

The formation of CO is evidence of incomplete combustion of carbon-based material. CO readily burns, having a flammability range of from 12.5 to 74.2 in air. Its most explosive concentration occurs at 29 . Concentrations in excess of 15 (150,000 ppm) are possible during a mine fire.

Mitchell (1990) provides a rule of thumb that, for every pound of coal burned, 0.5 cubic foot of CO is created. Knowing the CO concentration and the air quantity flowing through the fire area, the rate of burning coal can be determined:

$$R_{coal} \quad 2 \quad {}_{air} \left(\frac{CO_S}{1 \times 10^6} \right)$$

where:

R_{coal} rate of coal burning, lb/min

${}_{air}$ Entry air quantity, ft³/min

CO_S CO concentration, ppm

Table 4. Approximate coal burning rate

Sample	${}_{air}$ ft³/min	CO_Sppm	R_{coal}lb/min
1	6,700	7,490	100
2	7,000	17,920	250

In Table 4 the sampled CO gas levels changed significantly while the ventilation rate remained essentially the same. The resulting rate of coal burning more than doubled. This could indicate the change from an oxygen-rich fire to a fuel-rich fire. In any event, these results show that conditions are becoming more serious.

In other CO-related research, Timko and Derick (1995) have shown that changes in CO concentrations are directly dependent on ventilation air quantities and corresponding ventilation pressures at a particular location. When the CO level is decreasing, this could be due either to additional ventilation flowing over the affected area, or the heating is actually slowing. In spontaneous combustion-prone mines, once a heating begins, it rarely stops without ventilation changes or other controls being implemented.

Hydrogen

Hydrogen gas (H_2) is another key component in determining if fire exists. Hydrogen gas is most often generated as a byproduct of battery charging. It has been found in limited instances as strata gas. Hydrogen can also be liberated in elevated coal oxidation situations. It is detected at temperatures just below, and in high levels following, combustion. Hydrogen can also be created by an interaction between burning coal and water (so-called water gas reaction), at times in very high concentrations (approaching 15), and can actually exceed carbon monoxide levels. Because of its low (0.070) density relative to air, if adequate mixing is not taking place, H_2 will most likely be found at the roof.

Hydrogen is highly explosive. It is flammable in concentrations from 4 to 74 in air. Low H_2 levels begin to be detected at temperatures just below those required for active coal flaming.

Alkanes

Alkanes (Table 5) are commonly known as the methane series of gases. These are the products of the anaerobic decay of plants and are sometimes referred to as paraffins. Alkanes are saturated aliphatic hydrocarbons. A hydrogen atom unites with each available carbon atomic bond, and thus all carbon bonds are single bonds. In aliphatic compounds, the carbon atoms form open-chain molecules, rather than rings. Alkanes that are typically analysed through gas chromatography include methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and pentane (C_5H_{12}).

As methane concentrations increase, so do other alkanes. These are usually in descending concentrations relative to increasing density. When methane concentrations are very low, ethane may not be detected. When it is noted in possible fire samples, many confuse it as the fire gas ethylene. Alkane quantities tend to increase as temperatures rise.

Table . Density and flammability of alkanes

Al ane		Density relative to dry air	Flammability in air ( )
CH_4	Methane	0.55	5.0 to 15.0
C_2H_6	Ethane	1.05	3.0 to 12.4
C_3H_8	Propane	1.56	2.1 to 10.1
C_4H_{10}	Butane	2.07	1.8 to 8.4
C_5H_{12}	Pentane	2.49	1.5 to 7.8

Alkenes

Alkenes (Table 6) are unsaturated aliphatic hydrocarbons. These gases contain less than the maximum quantity of hydrogen atoms. Here carbon atoms are double-bonded, while all hydrogen atoms surrounding the carbon atoms are single bonded. The alkenes measured were ethylene or ethene (C_2H_4) and propylene or propene (C_3H_6).

Table 6. Density and flammability of alkenes

Al enes		Density relative to dry air	Flammability in air( )
C_2H_4	Ethylene	0.97	2.7 to 36.0
C_3H_6	Propylene	1.45	2.0 to 11.1
C_4H_8	Butylene	2.00	1.6 to 10.0
C_5H_{10}	Pentene[3]	2.40	1.4 to 8.7

Ethylene and propylene are byproducts of fire that are detected at approximately the same temperature. Normally, flaming combustion will take place prior to the detection of

[3] Pentene is a liquid below 30EC

either of these gases. In fires, alkenes can form from alkanes through the loss of hydrogen atoms by pyrolysis:

Large alkanes + HEAT Smaller alkanes + alkenes + H_2

Alkynes

Alkynes are highly unsaturated aliphatic hydrocarbons. In these molecules, the carbon atoms are triple bonded, while the hydrogen atoms surrounding the carbon atoms are again single bonded. The only alkyne that normally is analyzed is acetylene or ethyne (C_2H_2). The density of acetylene is 0.906, making it slightly less dense than air. The flammability range of acetylene in air is from 2.2 to 100 .

Other than using this gas for oxygen/acetylene cutting and welding underground, the only way this gas should be found underground is as a byproduct of combustion. Two more common ways to produce acetylene in coal mine fires are as follows:

Coal + HEAT |coke
and
Limestone + HEAT |CaO

coke + CaO +1100EC |CaC2 + H_2O + C_2H_2

$4CH_4 + O_2$. 820EC |C_2H_2 + 2CO + H_2

In the first reaction, coal and rock dust are heated to initially produce coke and calcium oxide (CaO). A higher temperature then causes these to react and form calcium carbide (CaC_2) and water, which finally combine to form acetylene. In the second reaction, methane and oxygen are heated to form acetylene, carbon monoxide, and hydrogen gas. Both reactions involve high temperatures. These will most likely occur in areas that are undergoing combustion and continuing to be ventilated because sufficient oxygen is necessary to permit temperatures to reach the required values. In mine fire situations, the acetylene concentration will usually be lower than alkene series concentrations.

Air-free ases

To eliminate the effects of sample dilution, one can determine changes in gas concentrations without the influence of oxygen. This can be accomplished with the following equation:

$$C_{AF} \quad \frac{C_S}{1-(0_2/20.95)}$$

where

C_{AF} Air-free gas concentration, ppm or

C_S Sampled gas concentration, ppm or

O_2 Oxygen concentration,

Air-free carbon monoxide levels found in Table 7 were obtained at a sealed mine immediately following a fire. These samples were taken at 24-hr intervals over six days. Air-free and sampled results closely parallel each other. Only when oxygen values approach ambient will air-free gas concentrations greatly differ from the actual sampled gas value because the denominator in the equation approaches zero when oxygen values move toward ambient.

Table 7. Air-free Carbon Monoxide, CO_{AF}

Sample Day	O_2	CO_s ppm	CO_{AF} ppm
1	1.84	19,971	21,894
2	1.15	23,267	24,618
3	0.42	11,575	11,812
4	0.57	8,816	9,063
5	1.08	8,857	9,338
6	1.88	4,863	5,342

Fire-related Equations

Several equations have been developed to aid in establishing the status of a mine atmosphere. These predictive models can be used to assist in determining:

1. If a fire exists,
2. What is burning,
3. If the fire is continuing to burn following sealing the affected area or mine, and
4. If the sealed atmosphere is presently explosive or will become explosive when ventilation commences.

In this section, a brief description of each equation is provided. Remember that these models are designed primarily to analyse trends and not to reach conclusions regarding the results of individual values. Only through long-term analysis can a realistic picture of the mine atmosphere be created.

These equations are most useful when specific parameters regarding sampling location and ventilation adequacy are known.

Is there a fire

Index of Carbon Monoxide

The index of carbon monoxide (ICO), or Graham's index (1914), is a dependable indicator of conditions underground because it eliminates the effects of sample dilution. The ICO is temperature dependent; i.e., its concentration rises with increasing temperature.

$$ICO \quad \frac{CO}{0.265(N_2) - O_2}$$

where

CO carbon monoxide, ppm

$0.265(N_2) - O_2$ Oxygen deficiency ( )O_2),

The ICO can signify increasing combustion if, after stabilising for a time, the values begin to rise. ICO levels will increase with increasing temperatures until an ignition occurs. Table 8 data were obtained at a bleeder evaluation point over several days. ICO values are increasing; gas sampling frequency should be increased and additional caution must be exercised. Once active combustion occurs, the rate of increase begins to slow and, in many cases, will stabilise.

Table 8. ndex of Carbon Monoxide, CO

Sample	O_2	N_2	CO ppm	ICO
1	17.16	78.99	49	12.99
2	17.54	79.35	45	12.90
3	17.71	79.32	44	13.29
4	18.51	79.01	51	21.01
5	18.56	79.07	55	22.98

In a like manner, once a mine area is sealed, ICO values will increase and will remain elevated until temperatures fall to near ambient levels. When the mine atmosphere approaches ambient levels, other indicators such as RATIO or the Hydrocarbon Ratio should be monitored along with the ICO because very small quantities of CO can be produced in normal oxidation and mineral desorption. This is common as the sealed atmosphere goes from smoldering combustion at slightly elevated temperature to ambient temperature oxidation. No minimum ICO value has been established to assist in determining when the atmosphere is safe.

Other problems exist for the ICO. When CO levels decrease and O_2 values remain the same or increase, values in the denominator are forced to zero because O_2 is no longer being consumed. This usually occurs when combustion has slowed. If corresponding CO levels are decreasing at a slower rate, the ICO may actually increase, indicating continued combustion. Fortunately, the ICO errs on the conservative side, suggesting that conditions are worse than actual. Another problem is that there is no single CO value, ratio, or index that can be applied uniformly to all mines. In some, small levels of CO will continue for extended periods. Conversely, Dougherty (1969) states that, once the area is again ventilated, the possibility of re-ignition does exist even though CO levels are low.

Index of Carbon Dioxide

Graham (1917) also developed a carbon dioxide index (ICO_2) to monitor elevated CO_2 levels:

$$ICO_2 \quad \frac{(CO_2 - 0.03)}{(100 - O_2)}$$

This equation, based on gas percentages, indicates elevated CO_2 values in an oxygen-free atmosphere. In a normal atmosphere, where only ambient CO_2 is generated, the ICO_2 provides the proportion of CO_2 to total inert gas and should approach zero. In a mine fire atmosphere, elevated CO_2 would be compared to total inert and gaseous byproducts of combustion.

If CO_2 is a product of combustion, an ICO_2 versus temperature plot will closely parallel an ICO versus temperature plot. Where no temperature information exists, an ICO/ICO_2 ratio can be developed.

Once ignition occurs, ICO_2 values increase and continue to increase as long as the temperature or fuel quantity increases. In sealed areas having no combustion, the ICO_2 value will also rise, but then stabilize with time. Table 9, using the same samples as shown at Table 8 data, shows increasing ICO_2 values, reinforcing the concern raised by the ICO results.

Table . ndex of Carbon Dioxide, CO_2

Sample	O_2	CO_2	$ICO_2 x10^{-2}$
1	17.16	1.41	1.70
2	17.54	1.35	1.60
3	17.71	1.40	1.66
4	18.51	1.43	1.72
5	18.56	1.47	1.77

What is burning

ones-Trickett Ratio

The Jones-Trickett Ratio (JTR), as described in Jones, Trickett (1954) determines sample reliability. It is based on the principle that the number of molecules of matter consumed in a fire is proportional to the number of molecules of gas produced, which is proportional to the volume of gas, assuming constant temperatures. It was originally developed to help researchers differentiate between gas or coal dust explosions. It has been adopted to mine fire situations.

The JTR equation, based on percent gas concentrations, is:

$$JTR \quad \frac{CO_2 + (0.75CO)-(0.25H_2)}{0.265\ (N_2) - O_2}$$

It varies with the type of fire, depending on the fuel. If the JTR is less than 0.4, no combustion exists. When the JTR is between 0.4 and 0.5, methane is the fuel. JTR values between 0.5 and 0.9 indicate that the fuel is coal, oil, conveyor belt, insulation, or urethane foam. If the JTR is between 0.9 and 1.6, wood is burning. Values of more than 1.6 generally occur only under controlled laboratory conditions. When JTR results above 1.6 are encountered during a possible mine fire, the gas chromatograph or sampling device should be examined for calibration or mathematical errors.

Table 10 continues the evaluation of the ICO and ICO_2 results previously shown. These five analyses should stimulate the operator to begin a more aggressive evaluation of possible heating sources.

Table 0. The Jones-Trickett Ratio, JTR

Sample	O_2	N_2	CO ppm	CO_2	JTR
1	17.16	78.99	49	1.41	0.37
2	17.54	79.35	45	1.35	0.39
3	17.71	79.32	44	1.40	0.42
4	18.51	79.01	51	1.43	0.59
5	18.56	79.07	55	1.47	0.62

Follo ing sealing, hat is the fire status

Relati e Intensity

Power industry engineers use the relative intensity (RI) equation to determine boiler and fuel efficiency, oxygen

excess or deficiency, water vapor production, and heat losses (Mitchell, 1984). RI measures the quantity of air available to burn a unit mass of fuel (11.6 lb of air are required to completely consume 1 lb of coal), the percentage of oxygen consumed, and the effect of combustion on temperature.

$$RI \quad \left(\frac{1-(0.0383\ O_2)}{N_2} \right) ICO$$

Adapting the RI to mine fire analysis, it is used to determine the proximity of the sampling location to the fire. It performs best when many sampling locations, such a boreholes, are spread throughout the mine.

All gas concentrations used in the equation are in percent. The RI equation is designed to show the location of the sampling point relative to the fire. If the RI increases, the fire is either growing or moving closer to the sampling location. Conversely, if the RI is decreasing, the fire is being throttled or moving away from the sampling location.

Table . Relative ntensity, R

Sample	O_2	N_2	CO ppm	ICO	RI
1	13.91	79.72	9540	1322	7.75
2	14.02	79.49	9460	1343	7.82
3	13.83	79.69	9550	1310	8.71
4	13.95	79.71	9610	1340	7.83
5	14.10	79.54	9540	1367	7.91
6	14.00	79.59	9690	1366	8.03

Table 11 data were remotely obtained over a six-hour period from a return entry. The mine was undergoing an uncontrolled spontaneous combustion event that had to be fought from the surface with high expansion foam. Relative to the fire itself, these results are inconclusive.

RATI

Litton (1986) developed RATIO to monitor a sealed mine atmosphere. It was designed to reduce the potential for reignition when a mine or section is reopened and oxygen is reintroduced. Only four gases are monitored: oxygen, carbon monoxide, methane, and ethane. The atmosphere is divided into three parts: air, methane and ethane, and residual gas. The only caveat is that this initial derivation of RATIO requires the oxygen concentration to be greater than 1 .

$$Air \quad a(O_2)$$

where

$$a \quad (100.000/20.946) \quad 4.774$$

Residual gas (R_g) is the volume percent of gas within a sealed coal mine after air and methane and ethane have been subtracted from the sample. R_g contains excess nitrogen (not part of air), products of combustion (CO, CO_2, H_2, and hydrocarbons), along with products formed by chemical processes not related to combustion.

$$R_g \quad 100.0 - Air - CH_4 - C_2H_6$$

The concentration of CO in parts per million of air within the residual gas is:

$$(CO)R_g \quad \left(\frac{CO_S}{R_g} \right) \times 100$$

where

CO_S sampled CO, ppm

From these values, the R-index (R_I) is created:

$$R_I \quad \frac{(CO)R_g}{R_g} \quad \left(\frac{CO_S}{(R)_g^2} \right) \times 100$$

If R_I remains constant, one of two things is occurring: sustained low-temperature combustion or a sustained low rate of ambient CO production. If there is combustion, the average R_I value will be higher than if ambient CO production is occurring because CO production increases with temperature.

Actual measured R_I is called $(R_I)_{act}$. A second R_I, the maximum equilibrium value, $(R_I)_{eq}$, is obtained by:

$$(R_I)_{eq} \quad 300 \left(\frac{R_g}{O_2} \right)^{-}$$

$(R_I)_{eq}$ represents the maximum equilibrium value of the R-index for a gas sample, if only ambient temperature processes are responsible for CO production.

A RATIO equation has been created to determine the state of a sealed area:

$$RATIO \quad \frac{(R_I)_{act}}{(R_I)_{eq}} \quad 1/3\ CO_S\ (R_g)^{-3/2}\ (O_2)^{-}$$

If the oxygen content is less than 1 the RATIO equation becomes:

$$RATIO \quad 1/3\ CO_S(R_g)^{-3/2}(O_2)$$

If RATIO is greater than one, ambient temperatures have not been reached; smoldering combustion or above-ambient temperature oxidation is occurring. This condition is considered unsafe for reentry. Table 12 data was obtained remotely from a panel that was sealed because of an uncontrolled fire. Samples were obtained every ten days to develop a long-term trend.

Table 2. Determining RAT O

Days	O_2	CH_4 ppm	CO ppm	C_2H_6	RATIO
0	13.89	0.38	9,540	740	4.45
10	12.69	2.61	8,750	700	3.68
20	10.80	3.41	5,440	640	1.83
30	9.45	3.93	3,970	660	1.19
40	8.83	4.20	1,950	580	0.56
50	6.69	5.10	820	490	0.21
60	5.81	5.23	635	440	0.16
70	5.34	5.49	352	410	0.09
80	2.25	5.42	140	410	0.04

If RATIO is less than, or equal to, unity, it is possible that ambient temperatures have been reached. Equilibrium exists only if the RATIO stabilises at a value less than one. Litton (1986) recommends the minimum time for the RATIO to remain stabilised at less than one is 30 days. If the RATIO remains below one for a time, then rises to a number greater than one, the 30-day period must begin anew. If the fire originated from spontaneous combustion, then consideration must include possible re-ignition once oxygen is reintroduced during recovery, even though the ratio indicates it is "out." Based on the fact that the RATIO has remained below one for forty days (Figure 1), these data show that the panel had stabilised fairly quickly and would not likely reignite when reentry was performed.

Figure . RAT O values over 80 days.

Hydrocarbon Ratio

Justin and Kim (1988) developed the hydrocarbon ratio after finding that low molecular weight hydrocarbon gases desorbed from coal in direct proportion to increasing temperature. Methane is readily liberated at ambient temperatures. The progression of gas desorption due to heating is carbon dioxide, carbon monoxide, hydrogen, ethylene, propylene, and acetylene. In effect, hydrocarbon concentrations increase with rising temperatures.

Knowing the desorption relationship resulted in development of the Hydrocarbon Ratio (R_1). It is defined as:

$$R_1 \quad \left(\frac{1.01\ (THC) - CH_4}{THC + c} \right) 1000$$

where

THC total hydrocarbon concentration, ppm[4]

CH_4 methane concentration, ppm

c constant, 0.01 ppm

R_1 is designed to equal zero when no hydrocarbons are detected, 10 when methane is the only measured hydrocarbon, and about 1,010 at the upper limit. The only limiting factor is that methane concentration must be greater than 20 ppm (0.002). Table 13 is taken from the same data shown in Table 12; samples were taken every ten days.

[4]Remember tha methane (CH4) should also be summed along with other hydrocarbons as part of the THC value

Table 3. Calculating the Hydrocarbon Ratio, R

Days	CH_4 ppm	H_2 ppm	C_2H_6 ppm	THC	R_1
0	3,800	5,300	740	9,840	624
10	26,100	3,840	700	30,640	158
20	34,100	1,950	640	36,690	81
30	39,300	670	660	40,630	43
40	42,000	80	580	42,660	25
50	51,000	5	490	51,495	20
60	52,300		440	52,740	18
70	54,900		410	55,310	17
80	54,200		410	54,610	18

For bituminous coal, R_1 values are closely dependent on temperature. Because of this, limits have been derived to aid in determining the temperature of coal being analysed. R_1 values from 0 to 50 indicate that normal oxidation is occurring. Values from 50 to 100 indicate possible elevated temperatures. Above 100, coal is undergoing elevated temperature oxidation.

Figure 2 shows the results of the same data presented in Figure 1. It is essentially reaching the same conclusion as the RATIO; i.e. over time the atmosphere is becoming more stable and active heating is less likely. It is still important to understand that, while active combustion within the section is slowing, sampling should continue at an enhanced rate.

Is the sealed atmosphere explosive could it become explosive once ventilation is restarted

Figure 2. Using R to determine atmospheric status.

xplosibility

Ideally, once an area is sealed,combustion begins to slow. Gas concentrations then begin to change. It is important to determine whether the atmosphere is explosive or has the potential to become explosive. Understand that during recovery, if combustion restarts and the atmosphere is explosive when mixed with air, an explosion will likely result. This type of problem is most often encountered when the

mine is being recovered and air is being reintroduced.

abetakis et al. (1959) created a diagram based on H.F. Coward's 1928 work that examined explosibility by comparing methane and oxygen. The abetakis diagram monitors explosibility of sealed atmospheres having a maximum hydrogen gas concentration of 50,000 ppm (5) and a 30,000 ppm (3) maximum carbon monoxide concentration. The values of all gases obtained for the following equations should be in percent. The diagram has three major elements: effective inert gases (EI), effective combustible gases (EC), and the ratio of methane to total combustibles (R):

$$EI \quad (N_2)_{excess} + (1.5 \text{ H } CO_2)$$

where

$$(N_2)_{excess} \quad (N_2)_{sampled} \text{ ! } (3.8 \text{ H } O_{2\ sampled})$$

The data for Tables 14 through 16 were the same as those collected for Tables 12 and 13. While the atmosphere based on the two previous equations appeared to be stabilising, the explosibility values will enable one to predict the likelihood of an explosion once fresh ventilation air is again introduced into the area.

Table 4. Effective nert, E

Day	N_2 sample	O_2 sample	N_2 excess	CO_2	EI
0	79.62	13.89	26.84	4.31	33.31
10	80.13	12.69	31.91	3.20	36.71
20	80.42	10.80	39.38	4.85	46.66
30	81.09	9.45	45.18	4.95	52.61
40	81.53	8.83	47.98	5.10	55.63
50	82.37	6.69	56.95	5.90	65.80
60	82.92	5.81	60.84	5.90	69.69
70	83.08	5.34	62.79	6.00	71.79
80	83.18	5.25	63.23	6.00	72.23

$$EC \quad CH_4 + (1.25 \text{ H } H_2) + (0.4 \text{ H } CO)$$

In the EC equation above, note that the values 1.25 and 0.4 are the lower explosive limit ratios of CH_4 to H_2 and CO, respectively.

The EI, EC, and R-values from Tables 14 through 16 can

Table . Effective Combustible, EC

Day	CH_4	H_2	CO	EC
0	0.38	0.5300	0.9840	1.44
10	2.61	0.3840	0.8750	3.44
20	3.41	0.1950	0.5440	3.87
30	3.93	0.0670	0.3970	4.17
40	4.20	0.0080	0.1950	4.29
50	5.10	0.0005	0.0820	5.13
60	5.23		0.0635	5.26
70	5.49		0.0352	5.50
80	5.42		0.0140	5.43

$$\underline{R} \quad \frac{CH_4}{(CO + CH_4 + H_2)}$$

Table 6. Ratio of Methane to Total Combustible, R

Day	CH_4	CO	H_2	R
0	0.38	0.9840	0.5300	0.2
10	2.61	0.8750	0.3840	0.7
20	3.41	0.5440	0.1950	0.8
30	3.93	0.3970	0.0670	0.9
40	4.20	0.1950	0.0080	1.0
50	5.10	0.0820	0.0005	1.0
60	5.23	0.0635		1.0
70	5.49	0.0352		1.0
80	5.42	0.0140		1.0

be plotted on the diagram shown in Figure 3. EI is plotted on the x-axis and EC on the y-axis. R-values, found in Table 16, vary between 0 and 1. Resulting data will fit into one of three areas: explosive, explosive when mixed with air, and nonexplosive. The specific area into which the sample will fit depends on R. In fact, when applying the R values to the Figure 3 diagram, it becomes obvious that, as the R values increase from 0 to 1, the area under the curve becomes smaller and the likelihood that specific gas concentrations will result in explosive mixtures becomes less.

Figure 3. Explosibility diagram

When the obtained data were plotted, they all fell into the "Nonexplosive Mixture" category. If one plotted the results chronologically, it became easier to determine if the atmosphere was moving toward or away from becoming explosive. In this case the atmosphere appeared to be moving away from potential explosibility.

Maximum Allowable xygen

Another alternative to determining if the atmosphere is inert or will become explosive upon introduction of ventila-

tion air is the Maximum Allowable Oxygen (MAO) analysis. If the measured oxygen concentration is below a specific value when compared to R, determined by the equation above, the air is either nonexplosive or may become explosive when mixed with air.

To determine the status of the atmosphere, calculate the R-value, refer to Figure 4, proceed horizontally across the chart from that number until intersecting the diagonal, and then continue vertically downward to find the corresponding MAO value. If the measured oxygen concentration is less than the MAO, the atmosphere cannot be ignited in its present state. Using only the MAO, care must be exercised when reintroducing air to the section because of the potential for the oxygen concentration to exceed the MAO. If the measured oxygen value is greater than the MAO, it is necessary to analyse the atmosphere via the Explosibility diagram.

Figure 4. Determining MAO

Discussion

Mine personnel should obtain gas samples at predetermined underground locations on a regular basis. This paper provides an overview of gas sampling equipment that should normally be on-hand and methodologies for taking samples. It gives instructions into various gases and gas-related equations that should be analysed and relates their changes over time to assist personnel in determining if a heating event is taking place.

Atmospheric status equations have either been developed specifically for the mining industry of adapted from other industries. These are tools to help personnel determine the condition of underground atmospheres. Some equations provide realistic analyses of atmospheric conditions as the mine or section continues to be ventilated, other equations are used once the mine or section has been sealed.

Prior to re-entering a sealed area, equations exist that can enable personnel to determine if the fire will rekindle once fresh air is reintroduced. In addition to the fire reigniting, an equation is available that assists personnel in determining if the atmosphere could become explosive when reintroducing fresh air.

In conclusion, mine personnel must understand that, except in specific instances, individual gas samples or equation results are less important than repetitive samples. It is much more important to group samples and analyse trends. Through conscientious sampling and analysis, the status of the atmosphere can more accurately be determined.

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Cover Picture:

Impala No.14 Shaft: Picture shows the surface bulk air cooler located near the main downcast shaft. The air cooler is a horizontal spray heat exchanger in which the air is forced through an intense spray of chilled water and heat exchange occurs directly across the large surface area of the spray drops. Cold water from the refrigeration machines is sprayed,collected and re-sprayed thus enabling high thermal efficiencies to be achieved. The air flow is 400 m³/s, the nominal duty is 15.2 MW cooling airto about 7°Cwb. This is achieved with water flow of 470 l/s at design condition of 4.5°C. The refrigeration plant serving the air cooler includes two large ammonia machines connected in parallel using Howden screw compressors driven by 1.85 MW motors.

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