Evaluation of Various Gas Mixtures in order to Avoid Disasters in Various Fire Zone Areas

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ABSTRACT
Provisions for periodic gas sampling so as to monitor and prevent hazardous accidents / disasters are made. This in turn has economical, social and ecological impacts involving loss of precious lives, hindrance in production and loss of machinery. Various effects due to the variation in the chemical composition of samples as compared to the normal composition of air are observed. These accidents may occur due to natural causes like lightning, grass or forest fires, self ignition leading to explosions/fires in hydrocarbons like coal, petroleum, natural gas(LPG,CNG), crude oil,wet gas or due to human errors in chemical industries or mines etc. Sample gas results are analysed with the basis of fire ratios or Explosibility triangle or Ellicott's Diagram. Using this triangle, the conclusion that the combustion will result in non-explosive (NE), explosive (E) or potentially explosive (PE) fire can be drawn.

Keywords
Gas sampling, fire ratios, Explosibility triangle, spontaneous combustion.

1. INTRODUCTION
Dangerous substances are any substances used to present at work, that could, if not properly controlled, cause harm to people as a result of fire and explosion. Large fires can be started in small areas with simple materials. Explosive atmospheres can be caused by flammable gases, mists, or vapours or by combustible coal dusts. Fire is the rapid oxidation of the material in the exothermic chemical process of combustion, releasing heat, light and various reaction products.

When certain chemicals, gases, and other substances are kept in an unstable state or are exposed to heat or fire, they may pose the risk of exploding. Explosions that are commonly reported includes Propane, Industrial, Refinery, Residential gas, Boiler, Natural gas, Petroleum, Fuel tanks, Coal dust. People who are walking, standing or working near the site of blast may suffer injuries resulting from flying debris, impact injuries, burns, heat/ smoke/ chemical inhalation, and other trauma. Explosions and blasts may be caused by improper transport, storage, or treatment, and will result in physical injuries and major damage to properties and infrastructures like roads, pipelines, electric lines, bridge supports, buildings and homes, that are engulfed in flames.

2. METHODOLOGY
Various effects due to the variation in the chemical composition of samples as compared to the normal composition of air are observed. The normal composition is as follows:

Chemical Composition of Air		
Name	Symbol	% by volume
Nitrogen	N2	78.084 %
Oxygen	O2	20.9476 %
Argon	Ar	0.934 %
Carbon Dioxide	CO2	0.0314 %
Neon	Ne	0.001818 %
Methane	CH4	0.0002 %
Helium	He	0.000524 %
Krypton	Kr	0.000114 %
Hydrogen	H2	0.00005 %
Xenon	Xe	0.0000087 %

Figure 1 Chemical Composition of Air

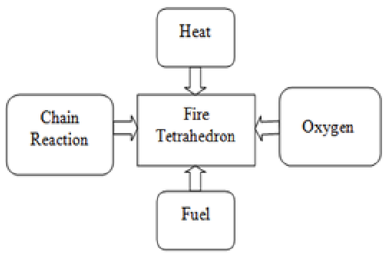

Figure 2 The fire tetrahedron

Fires start when a flammable or a combustible material in combination with the sufficient quantity of an oxidizer such as O_2 gas or another oxygen rich compound (though non-oxygen oxidizer exists that can replace O_2) is exposed to a source of heat or an ambient temperature above the flash point for the fuel/oxidizer mix, and is able to sustain rate of rapid oxidation that produces a chain reaction. This is called as fire tetrahedron.

3. BLOCK DIAGRAM

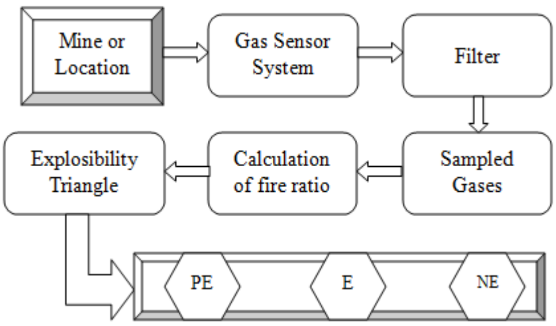

Figure 3 Block Diagram

Sample gasresults are analysed with the basis of fire ratios or Explosibility triangle or Ellicott's Diagram with both. Using this we can determine various Explosibility levels such as PE,NE or E.

4. DEVELOPMENT OF HEATINGS[4]

Heating's are difficult to discover and are often not detected until well advanced. They may commence as small as football size shape, giving off low volume of gas in goaf, which is difficult to detect.

5. LOCATION OF HEATINGS[4]

Prevention, early detection, and control of spontaneous combustion risk will not be effective unless the potential hazard and locations are correctly identified.

6. DETECTION[4]

Early indication of the onset of spontaneous combustion will most often provide time for action to be taken to control the heating before the need for people to be withdrawn from the site.

It is important to realize that all the time taken for heating to develop to a dangerous stage is not available because there is no way to be certain when the heating has started. Time will elapse before heating is first detected. Only the time from when the heating is first detected to when men must be withdrawn is available for effective action. These may be weeks or even days depending upon the situation and environmental conditions.

Early warning techniques include detection of rise in oxygen in sealed area and unplanned changes in ventilation pressure and flow. These techniques may provide an opportunity for early warning of spontaneous combustion rather than waiting for the detection of product of combustion.

Figure below shows the relatively small window of opportunity to detect and control a heating if reliance is safely upon detected and interpretation of gaseous product of spontaneous combustion.

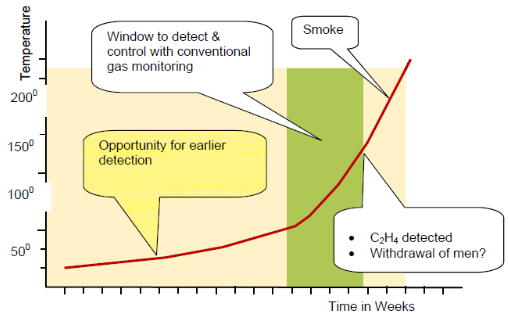

Figure 4 Incubation period of heating

7. METHOD OF DETECTION[4]

The observation of physical signs is an important method of detection. The physical signs are:

1. Rise in temperature
2. Sweating(approx 100°C)
3. Smell(approx 110°C)
4. Haze
5. Smoke(approx 300°C)
6. Gas level
7. Air flow and direction

The atmosphere in area may be sampled by means of real time sensors, tube bundle lines and sampling bags.

8. GAS MONITORING SYSTEM[4]

A comprehensive gas monitoring system is an effective tool for the detection and monitoring of spontaneous combustion. Monitoring system include:

1. Tube bundle system with analysers located on the surface.
2. Real time(telemetric) system
3. Routine inspection using portable devices.
4. Gas bag sampling for analysis mine or by the third party provided.
5. Gas chromatography system.

9. INTERPRETATION OF RESULTS

The trends in gas levels are important. Are the levels rising, steady or falling? Using gas values alone is problematic. Ratios are much better indicators. There are number of ways certain gases and their presence can be interpreted to determine the presence of heating and its stage of development.

FIRE RATIOS[2],[6]

Interpretation of gas analysis results systematically calls for a powerful tool known as fire indices. Since the beginning of the 20^{th} century many ratios and composites of gas concentration have been suggested to assist in the interpretation of fire gases.

The observation of the build up of combustion gases alone may be risky in order to determine the spontaneous combustion. These ratios are supposed to assist in the detection of heating as early as possible and to state the progress most accurately. To be effective, the gas analysis used by these ratios must be rapid, accurate and precise.

OXYGEN DEFICIENCY[1],[5]

Several of the fire ratios commonly calculated from results use Oxygen deficiency. It is the amount of oxygen consumed/ removed by any activity and is often determined using the following equation:

Oxygen deficiency = 0.265* $N_2 - O_2$

This equation is based on the assumption that nitrogen, being an inert gas, will not be consumed nor will it be created. If the initial gas entering the area under investigation had a fresh air ratio of 20.95 % oxygen to 79.02 % nitrogen (20.95/79.02= 0.265), then the initial oxygen concentration can be determined using the amount of nitrogen determined to be present in the sample. Ratios incorporating oxygen deficiency will underestimate if there is more than one source of oxygen deficiency[5].

There are well documented ratios and indices that are used for monitoring the progression of heating, the following are as follows:

1. Graham's Ratio
2. CO/CO_2 Ratio
3. CO make
4. Young's Ratio
5. Jones and Trickett's Ratio
6. Litton Ratio
7. Willett's Ratio
8. Air free analysis
9. H_2 /CO Ratio
10. C/H Ratio

9.1 Graham's ratio [2],[4]

Graham's Ratio (GR) is useful in low oxygen environments such as goaves, and is also applicable in ventilated roadways. This ratio generally expressed as percentage, represents the fraction of the oxygen absorbed as a result of heating or fire which appears as carbon monoxide.

$$GR = 100 * \frac{CO}{(0.265 * N2) - O2}$$

Values of GR quoted in a number of technical references are

- ≤ 0.4 per cent indicates normal value
- 0.5 per cent indicates necessity for a through checkup
- 1 per cent indicates existence of heating
- 2 per cent indicates serious heating approaches active fire
- 3 per cent and above indicates active fire with certainty
- Values of GR ≥ 7 may occur for blazing fire

The trend of the readings here, is more important than absolute values, with an increasing trend indicating increase in temperature within the fire.

9.2 Young's ratio [2],[4]

Young's ratio is same as Graham's ratio except that CO is replaced by CO_2 as the indicator of oxidation. Because of the size of the CO_2 concentration it is not usually multiplied by 100 and thus is a fraction not a percentage as in Graham's Ratio. Carbon Dioxide produced as a percentage of oxygen absorbed is considered as Young's Ratio or CO_2 /O_2 deficiency ratio.

$$YR = 100 * \frac{CO2}{(0.265 * N2) - 02}$$

If the value of this ratio is below 25 it is considered to be indicative of superficial heating. If it is more than 50 it should be corroborated with other fire indices to rule out or confirm a high intensity fire.

9.3 CO/CO_2 Ratio [2],[4]

It is suitable for both sealed and fresh air heating. It is generally expressed in percentage.

This ratio is independent of oxygen deficiency and so overcomes a lot of problems associated with other ratios that are dependent on that deficiency. It indicates the completeness of the combustion or oxidation. This ratio has a significant advantage that it is unaffected by inflow of air, methane or injected nitrogen. The index increases rapidly during early stages of heating, but the rate of increase slows at high temperature. This index can be used only when no carbon dioxide occurs naturally in the strata.

- > 2 per cent indicates active fire in the adjacent zone.
- ≥ 13 per cent indicates blazing fire.

9.4 Jones and trickett ratio [2],[4]

This ratio serves as an indicator of the type of fuel involved in any fire or explosion. Jones and Trickett developed this ratio for determining whether methane or coal dust has been involved in a mine explosion.

$$JTR = \frac{[CO2 + (0.75 * CO) - (0.25 * H2)]}{(0.265 * N2) - O2}$$

- <0.4 normal
- <0.5 methane fire possible
- < 1.0 coal fire possible
- > 1.6 impossible

10. ANALYSIS OF EXPLOSIVE STATE OF ANALYZED GAS MIXTURE[2]

After knowing the status of heating the next question is whether the gas mixture is explosive in nature. The gas mixture becomes explosive when there is rising concentration of combustible gases and falling concentration of oxygen.

The analysis utilises the concept of converting the methane, hydrogen and carbon monoxide in the atmosphere to an effective combustible content and the carbon dioxide and nitrogen to an effective inert content. The methodology to calculate whether the gas mixture is explosive or not, is calculated using the following formulae:

1. Percent Excess N_2 = Percent N_2 in the sample – Percent Normal N_2
2. Percent Normal N_2 = 3.8* Percent O_2 in the sample
3. Effective Inert = Percent Excess N_2 + 1.5* percent CO_2
4. Effective Combustibles = Percent CH_4 + 1.25 * Percent H_2 + 0.4 * Percent CO
5. Total Combustibles = CO + CH_4 + H_2
6. R = CH_4/ (CO + CH_4 + H_2)

11. CONCLUSION

Different ratios to determine the Explosibility of gas mixtures are seen. This in turn will let us know that the resulting explosion due to the mixture will be either a potential explosion or not. This can be very helpful to save the resources nearby. These ratios include Graham's Ratio, Young's Ratio, CO/CO_2 Ratio, Jones and Trickett Ratio. These ratios are used to determine the heating status of gases. Care must be taken when calculating oxygen deficiencies to ensure that the calculation is correct and representative for the sample and analysis technique.

12. FUTURE WORK

Explosibility triangle using various gas samples can be plotted. After that analysis of the Explosibility triangle can be done and then Explosibility of air mixture whether it is Potentially Explosive, Non-Explosive or Explosive can be determined.

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