# The Influence Analytical Techniques and Uncertainties in Measurement Have on the Assessment of Underground Coal Mine Atmospheres

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## Abstract

With the increased automated monitoring and bag sampling regimes for analysis by mine site gas chromatograph (GC) seen in the Queensland mining industry in the past ten years, it is important that the strengths, weaknesses and applicability of each technique is understood by those both interpreting and reliant on the results.

Slight variations in measurement can have a significant impact on commonly used indicating ratios and calculations, rendering them unreliable. This is particularly the case for Graham's Ratio calculations determined for areas of minimal oxygen deficiency, including return airways for which there is a requirement in the Queensland Mining Regulations.

Failure to perform a complete analysis by GC of atmospheres generated during coal fires or heatings can lead to wrongly assessing the atmosphere to be inert, when in fact it could be explosive or fuel rich due to the generation of percent levels of carbon monoxide and hydrogen.

## Introduction

Queensland's underground coal mining industry has seen a dramatic increase in the amount of automated gas monitoring and bag sampling over the past ten years. This has resulted in the generation of more gas data than ever before. An average control room receives real time gas data from up to forty points, each point measuring up to four gases, updated every thirty seconds with data saved every ten minutes. Tube bundles are generally monitoring between twenty and forty points, updating a single point every ninety seconds. Depending on the status of the underground environment, ten bags or more may be analysed by GC each day.

What should we do with all of this data? Does it all tell us the same things? Which technique is the best? It is important that the strengths, weaknesses and applicability of each technique is understood by those both interpreting and reliant on the results.

## Monitoring Techniques

Real time sensor systems (telemetric systems) are ideal for telling us what is happening now. The sensors must be located where the gas needs to be measured, and the measurement signal is sent to the surface. This means having multiple sensors underground, and that these sensors are exposed to the harsh underground environment which is not ideal for precise analytical measurements. This is not really a major problem as these systems are used to detect step changes, such as the onset of a fire, a sudden increase in a seam gas in the general body or reduction in oxygen. They offer real time warning and are the best system for identifying a sudden event such as a belt fire. The situation is reported when it happens. Generally, sensors included are methane, carbon monoxide, carbon dioxide, and oxygen.

These types of sensors employed underground tend to have limited measuring ranges: carbon monoxide is often only capable of being measured up to 50ppm, methane to 5% and carbon dioxide to several percent. This range is fine while no problems exist, and indeed to alert the onset of a problem. But if a fire or other major incident involving generated gases occurs, these sensors may quickly reach full scale and be unable to return a true indication of the concentrations.

Due to the environment these sensors are in and their characteristics, they are not as useful for long term trending as the other techniques. Most of these sensors require the presence of oxygen to work and are therefore unsuitable for monitoring areas of low oxygen concentration such as a goaf.

Tube bundle systems, on the other hand, are suited to long term trending (provided the system is suitably maintained). Very good analytical equipment is available and can be housed in dedicated air conditioned rooms on the surface with the samples dried and passed through particulate filters prior to entering the analyser. Generally systems are set up to measure oxygen, carbon monoxide, carbon dioxide and methane. Given their ability to measure carbon monoxide down to 1ppm, the long term stability of these analysers and the frequent sampling, this technique is best for long term trending of carbon monoxide, and carbon monoxide make, to identify a spontaneous combustion event. With respect to measuring range, it is normally only carbon monoxide that presents problems, with most systems capable of measuring to only 1000ppm. Because methane and oxygen concentrations can be measured over all expected concentrations ranges, this technique is the best for automated monitoring of explosibility of an area so long as a fire or heating doesn't exist. This technique is best for monitoring explosibility during a routine sealing operation and for the early onset of any spontaneous combustion event.

To get this improved stability and analytical capability, we sacrifice the immediate availability of the results. The samples need to be drawn to the surface prior to being analysed, and this means the data being generated can be from samples collected from over an hour before. There is only one bank of analysers, so only one sample is analysed at a time. Depending on the number of tubes in the system and the programmed sampling sequence, each point may only be sampled once every thirty to sixty minutes. Add this to the time taken to draw the sample from underground, and it is obvious this technique is not suitable for the instantaneous detection of an incident such as a fire.

Because the analysers in these systems rely on infrared absorbance and paramagnetic attraction the gas matrix is not important, making this technique suitable for the analysis of gases from oxygen depleted areas such as goaves. What must be remembered is that the measurement of oxygen using paramagnetic analysers is flow rate dependent and the flow from each tube must be balanced to be the same. Otherwise it is possible that two locations could in fact have the same oxygen concentration, but because of more resistance in one of the tubes, the flow through the analyser is at a lower flow rate and as such results in a lower reading than a location with the same concentration but flowing through the instrument at a faster rate. The importance of getting the oxygen measurement correct has significant implications in calculating ratios utilising oxygen deficiency as discussed latter.

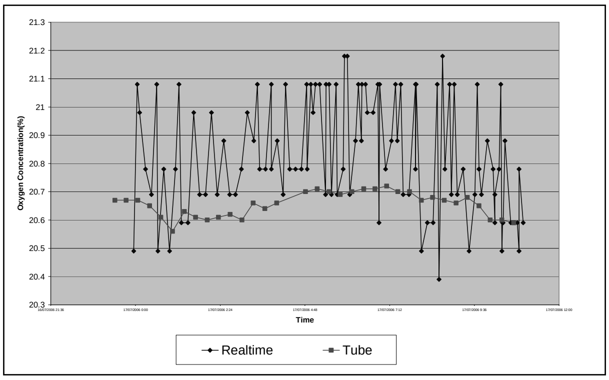
Too often the maintenance of the tubes is overlooked and the monthly leak testing identified in Australian Standard "*AS2290.3 Electrical equipment for coal mines – Maintenance and overhaul Part 3: Maintenance of gas detecting and monitoring equipment."* is not performed or not done as stated by the standard. If maintenance follows the method outlined in the standard, it is not only possible to confirm that no leaks exist but also determine an approximate time taken for a sample to reach the surface. The knowledge of the draw times of each tube is critical to adequately assess what is happening and how long ago it actually happened in an emergency situation.

Another strong point of real time sensors and tube bundle monitoring is that the monitoring points are at fixed locations, resulting in consistent automated sampling/measurement. When bag samples are collected for subsequent GC analysis, variations in results and trends can often be attributed to not collecting samples from exactly the same locations, or poor sampling techniques.

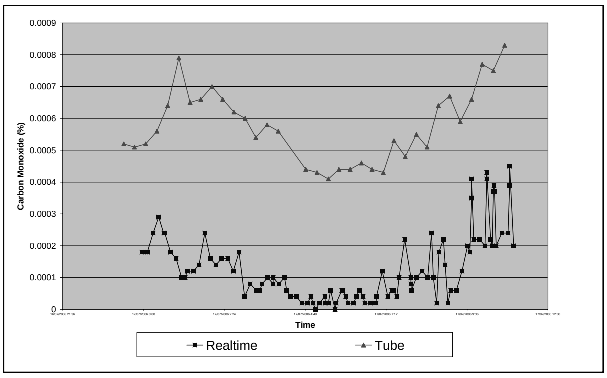
The use of a GC expands analytical capabilities to include gases crucial in the interpretation of spontaneous combustion events, particularly ethylene and hydrogen. The GC provides a complete analysis of the gases expected underground and is the only one of the three techniques capable of measuring hydrogen, nitrogen, ethylene and ethane. Similar to the tube bundle, problems exist with bringing the samples to the GC. The significance of time delays in getting results is dependent on what the results are being used for. GC is not going to be suitable for detection of a belt fire because of the time delay between collection of the sample and analysis, but the delay is acceptable for confirmation of other results or for evidence and trending of spontaneous combustion indicators. The GC is not the best analytical technique for low concentrations of carbon monoxide, therefore this technique is not the preferred method for determination of carbon monoxide makes. However, during a significant spontaneous combustion event, fire or following an explosion, it is the only technique that will allow us to make an accurate determination of the explosibility of the underground environment. Like the tube bundle system, the gas matrix of the sample does not affect GC analysis. So long as appropriate calibration gases are available, this technique is capable of measuring gases at any concentration above their detection limit. This eliminates the problems seen with the other techniques, particularly for carbon monoxide concentrations greater than 1000ppm.

Graphs 1-6 compare measurements using different techniques for the same location. It can be seen In Graph 1, that oxygen measurements were much more stable using the tube bundle than for the real time sensor which regularly varied by more than 0.3% (absolute) between measurements. Although the carbon monoxide concentrations in Graph 2 were different, the trend over the 24 hours was the same for the two techniques. Although slight differences in absolute concentrations are evident and the difference in the amount of data collected by the techniques is significant, the tube bundle data and GC data (Graphs 3-6) show very good agreement over a one month period, reflecting increasing and decreasing trends.

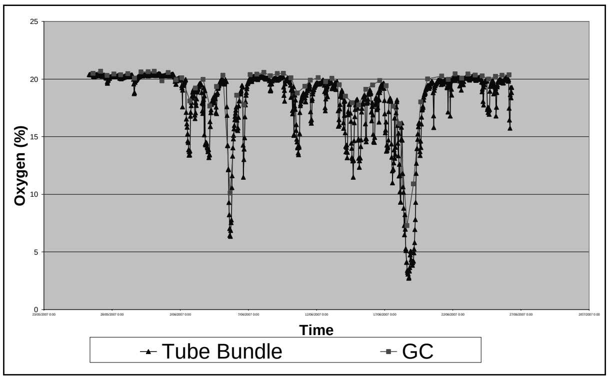
**Graph 1 Real Time vs Tube Bundle $O_2$ Data**



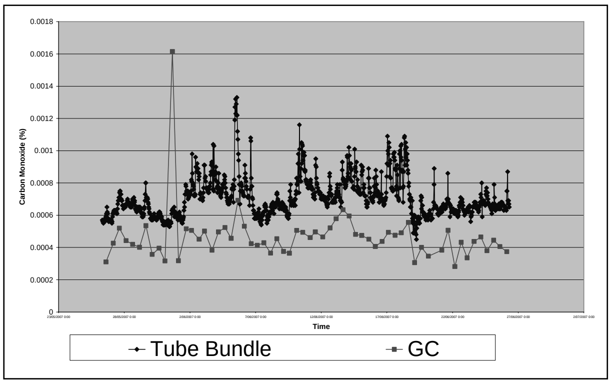
**Graph 2 Real Time and Tube Bundle CO Data**



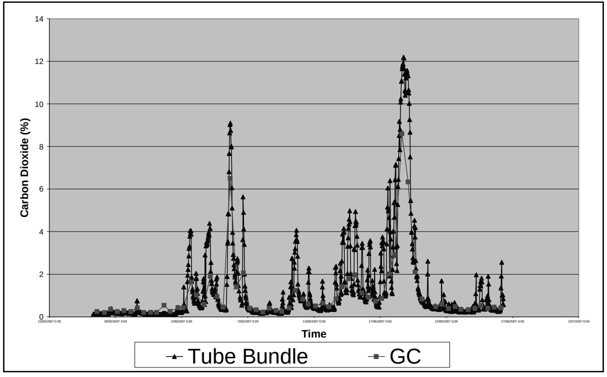
**Graph 3 GC vs Tube Bundle $O_2$ Data**



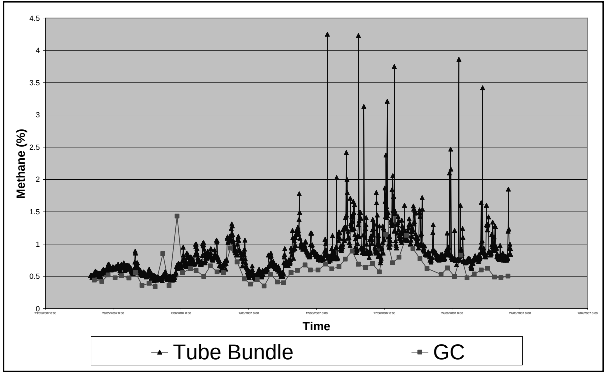
**Graph 4 GC vs Tube Bundle CO Data**



**Graph 5 GC vs Tube Bundle $CO_2$ Data**



**Graph 6 GC vs Tube Bundle $CH_4$ Data**



### Oxygen Deficiency

Several of the ratios commonly calculated from results generated from all three techniques described above and used to determine the status of any spontaneous combustion activity require determining the oxygen deficiency. Oxygen deficiency is the amount of oxygen consumed/removed by any activity and is often determined using the following equation:

Oxygen deficiency = 0.265 x $N_2 – O_2$ **(Equation 1)**

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 ($O_2$) to 79.02% nitrogen ($N_2$) (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. The use of the fresh air nitrogen concentration of 79.02% includes argon in the amount and is used for techniques that are unable to differentiate the two gases. Use of this equation is only valid for samples where the initial gas has the same oxygen to nitrogen ratio as fresh air. Because we are using the measured nitrogen to determine the initial oxygen concentration, we eliminate most problems with dilution because the measured nitrogen has also been diluted.

This equation can be used effectively only when the oxygen deficiency is not great. Because analysis is done on a percentage volume basis, if oxygen is being consumed/removed and we don't have anything replacing it, although the actual number of nitrogen molecules does not increase, the percentage of the gas that is nitrogen does. This causes problems with the calculation of the oxygen deficiency using this method, by over estimating the initial oxygen concentration and therefore the oxygen deficiency. Examples from real mine incidents highlighting this are outlined in Table 1.

**Table 1 Oxygen Deficiency Calculations**

| **Measured Oxygen %** | **Measured Nitrogen %(including Argon)** | **Calculated Initial Oxygen % (0.265x$N_2$)** | **Calculated Oxygen Deficiency % (0.265x$N_2$- $O_2$)** | **Calculated Oxygen Deficiency % (20.95- $O_2$)** |
|---|---|---|---|---|
| 2.334421 | 81.84362 | 21.68856 | 19.35414 | 18.61558 |
| 9.150444 | 80.43649 | 21.31567 | 12.16523 | 11.79956 |
| 15.7 | 83.1 | 22.0215 | 6.3215 | 5.25 |
| 8.1 | 89.1 | 23.6115 | 15.5115 | 12.85 |

Table 1 shows that when using Equation 1 in cases where significant oxygen deficiencies exist, the calculated initial oxygen can be greater than that in fresh air (20.95%), an obvious problem. The effect of this over estimation of oxygen deficiency is an under estimation of ratios using oxygen deficiency as the denominator (such as Graham's Ratio).

Graham's Ratio is used to measure the intensity of a heating. It is a measure of how much carbon monoxide is produced for how much oxygen is used up to produce the carbon monoxide.

Neither tube bundle nor real time systems measure nitrogen. To calculate oxygen deficiency using Equation 1 (or any other calculation that requires nitrogen input) using these measurement techniques, nitrogen is calculated by summing the measured oxygen, carbon monoxide, carbon dioxide and methane, and assuming that all of the remaining gas is nitrogen.

There are problems associated with inferring the nitrogen concentration by difference when it is used for calculations using oxygen deficiency. Oxygen analysers used in mining are required to meet tolerances of +/- 0.2% (according to AS2290.3). Therefore, a measured oxygen concentration of 20.7% could be as low as 20.5% or as high as 20.9%. If a sample returned concentrations of 10ppm CO, 0.1% $CO_2$ and 20.9% $O_2$, the calculated nitrogen concentration would be 79.2% (by difference). As the oxygen could be between 20.5% and 20.9%, the nitrogen (by difference) could be between 79.4% and 79.0%.

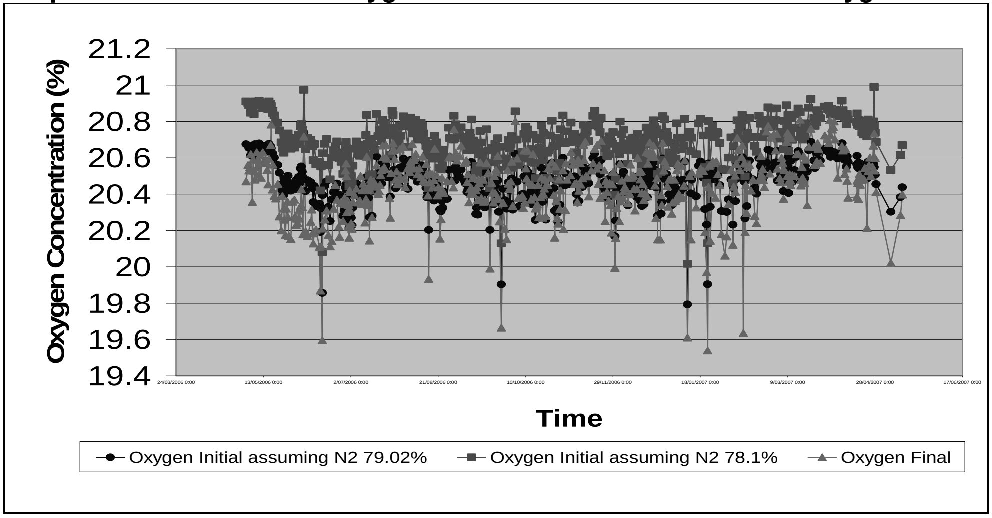
Calculating Graham's Ratio using:
$GR = 100 \times CO / (0.265 \times N_2 – O_2)$ **(Equation 2)**
Graham's Ratio would range between:
$GR = 100 \times 0.001 / (0.265 \times 79.4 - 20.5)$ and $GR = 0.001 \times 100 / (0.265 \times 79.0 - 20.9)$
$= 0.1 / (21.04 - 20.5)$ $= 0.1 / (20.94 - 20.9)$
$= 0.1 / 0.54$ $= 0.1 / 0.04$
= **<u>0.18</u>** = **<u>2.86</u>**

If the interpretation was done in isolation on this sample, without allowing for the limits of accuracy of the analysers, the conclusion could vary between normal conditions and open fire, according to literature values for Graham's Ratio.

GC is the only method of analysis that actually measures the nitrogen, giving added confidence in ratio calculations in light of the above. It must be noted that if oxygen deficiencies are being calculated using GC results, Equation 1 (and Equation 2) must be modified if the results determine argon separate to nitrogen. Equation 1 assumed the oxygen to nitrogen ratio in fresh air to be 20.95:79.02 (0.265). In reality, 0.9% of that nitrogen total can be attributed to argon and if the two are being reported separately, Equation 1 should be modified to:
Oxygen deficiency = $0.268 \times N_2 - O_2$ **(Equation 3)**
Because without including argon with the nitrogen, the fresh air ratio is 20.95% oxygen to 78.1% nitrogen (20.95/78.1=0.268).

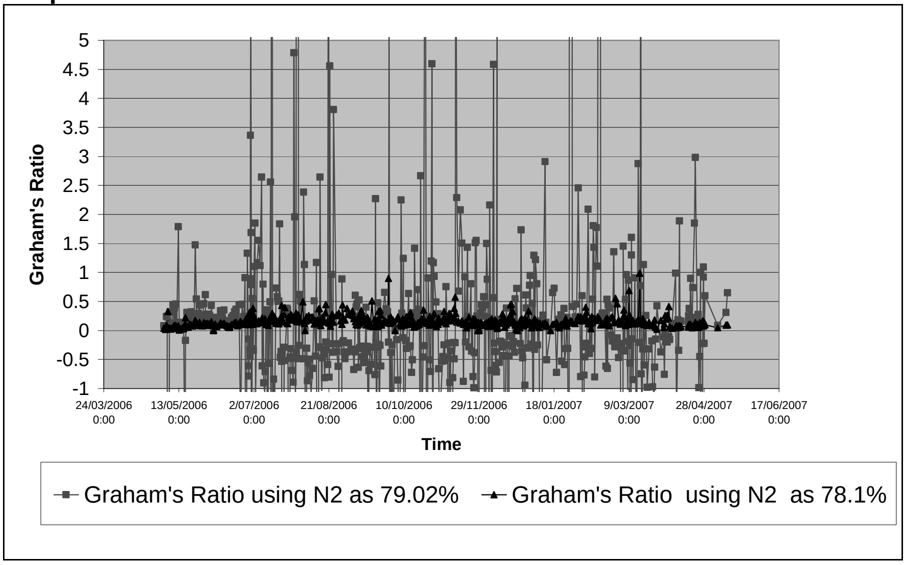
If this is not taken into account, oxygen deficiencies and subsequent indicating ratios will be incorrect. Graph 7 shows that by using the factor of 0.265 on samples that have been analysed with separate results for nitrogen and argon (GC), it is possible in some cases to calculate initial oxygen concentrations less than the measured final oxygen concentrations — an obvious impossibility.

**Graph 7 Calculated Initial Oxygen Concentrations vs Measured Oxygen**



The effect that this incorrect oxygen deficiency has on a calculation such as Graham's Ratio can be seen in Graph 8.

**Graph 8 Graham's Ratio**



Because of the problems with the oxygen deficiency when using the factor of 0.265, a lot of negative and very high values for Graham's Ratio are obtained. Values appear to be randomly between serious fire and impossible and do not compare well with the Graham's Ratios calculated using the factor of 0.268. When Graham's Ratio is calculated incorrectly (using the factor of 0.265) for results that differentiate between nitrogen and argon, generated data may not offer any useable information to those reviewing the data. The same problem exists for any ratio/calculation that relies on the ratio of oxygen to nitrogen.

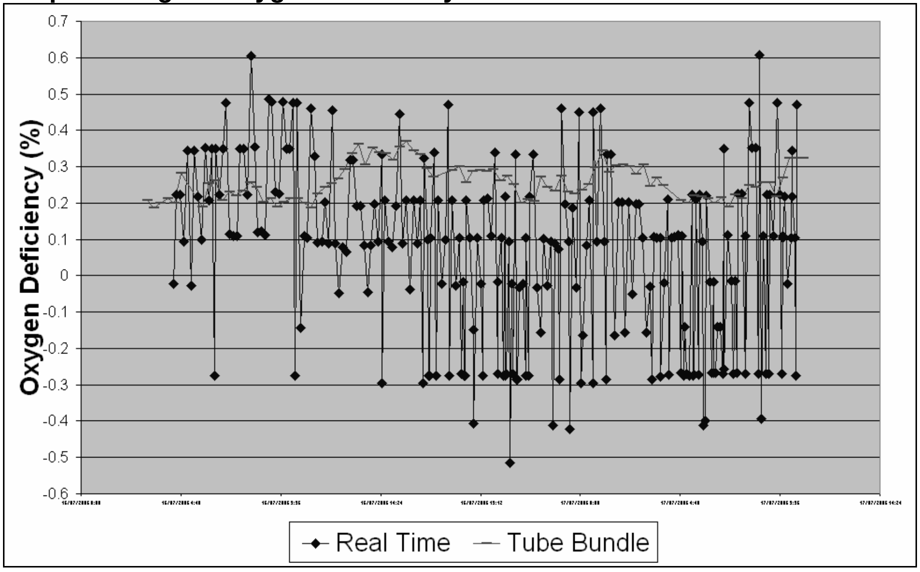
One of the reasons the Graham's Ratio data is so erratic in Graph 8 for the calculations using the factor of 0.265 is that the actual calculated oxygen deficiency is so small.

Mitchell (1996) states that this ratio would be misused and could lead to incorrect interpretation when the oxygen deficiency is less than 0.3.

Strang and MacKenzie-Wood (1985) also state, "This like any calculation, is subject to limits of analytical errors and it is generally considered that oxygen deficiency of 0.2 percent or less would introduce gross errors. This point is made so that caution can be exercised in interpreting results when such low oxygen deficiencies occur."

This documented problem associated with calculating Graham's Ratio when only small oxygen deficiencies exist has implications for Queensland's underground coal mines. Part 7 of The Coal Mining Safety and Health Regulation (2001) outlines the requirement for mines to have a gas monitoring system providing continuous monitoring of methane, carbon monoxide, carbon dioxide and oxygen at stated locations (including the return airway of each ventilation split). The gas monitoring system must also automatically detect and calculate the values of, amongst other things, the ratio of carbon monoxide to oxygen deficiency (Graham's Ratio). The requirement for continuous monitoring as opposed to continual, which was previously stated, infers the requirement for a real time system. As evidenced in the included graphs, the variation in oxygen concentration using this type of system results in problems with calculating the oxygen deficiency. The ventilation quantities used to ventilate modern longwall mines mean that the oxygen deficiencies seen in tailgate returns are often less than 0.3% (Graph 9) and therefore not sufficient to provide a reliable assessment. That is not to say that Graham's Ratio may not be useful in some instances at these locations, but, in general, the lack of oxygen deficiency and the variation in measurement of this technique results in a lot of unreliable data.

**Graph 9 Tailgate Oxygen Deficiency Real Time vs Tube**



Graph 9 shows that over a 24 hour period the majority of samples as analysed by the tube bundle returned oxygen deficiencies of less than 0.3%. Oxygen deficiency calculations from the real time measurements also returned a majority of values less than 0.3 with a significant amount actually negative.

It needs to be noted that oxygen deficiency is not just a reduction in oxygen concentration caused by dilution with seam gases but the "consumption" of oxygen. The ratios that use this parameter are determining how much products of combustion are being produced for how much oxygen is being used. As the coal gets hotter, the efficiency of the reaction increases, with more products produced for less oxygen consumed. If another monitoring point or sample (e.g. a longwall panel intake) is used as the initial oxygen, any dilution with seam gas is seen as oxygen deficiency and will over estimate oxygen deficiency and subsequently under estimate any indicating ratios using oxygen deficiency as a denominator. Table 2 demonstrates this with a sample that has been diluted by increasing amounts of methane but with no change in oxygen "consumption" or production of carbon monoxide (only dilution). The initial oxygen has been taken as the fresh air oxygen concentration (20.95%).

**Table 2 Graham's Ratio Calculations**

| Introduced Methane | Initial Oxygen Concentration (%) | Oxygen Measured in Sample (%) | Carbon Monoxide Measured in Sample (%) | Graham's Ratio 100xCO/ (20.95-$O_2$ Measured) |
|---|---|---|---|---|
| 0 | 20.95 | 20.8 | 0.0005 | 0.333 |
| 3% | 20.95 | 20.8x0.97 = 20.18 | 0.0005x0.97=0.00049 | 0.063 |
| 6% | 20.95 | 20.8x0.94 = 19.55 | 0.0005x0.94=0.00047 | 0.034 |

These results highlight how much ratios can be underestimated if oxygen deficiency is calculated using an actual oxygen measurement for initial oxygen, and the final oxygen concentration is affected by dilution. Often monitoring systems (particularly tube bundle) reference another point for the initial gas concentrations, making them prone to the errors seen in Table 2. To overcome this problem oxygen deficiency can be calculated as:

$O_2$ deficiency = $(N_2f/ N_2i)xO_2i – O_2f$ **(Equation 4)**

and GR =$100x(COf-(N_2f/ N_2i)xCOi)/((N_2f/ N_2i)xO_2i – O_2f)$ where i is initial and f is final **(Equation 5)**

Table 3 shows how Equation 5 overcomes problems caused by dilution with Graham's Ratio when using initial oxygen concentrations. Initial concentrations of 20.95% oxygen, 79.02% nitrogen and 0ppm carbon monoxide have been used.

**Table 3 Graham's Ratio Calculations**

| Introduced Methane | Measured Nitrogen Concentration (%) | Oxygen Measured in Sample (%) | Carbon Monoxide Measured in Sample (%) | Graham's Ratio Using Equation 5 |
|---|---|---|---|---|
| 0 | 78.8 | 20.8 | 0.0005 | 0.55 |
| 3% | 78.8x0.97=76.44 | 20.8x0.97 = 20.18 | 0.0005x0.97=0.00049 | 0.55 |
| 6% | 78.8x0.94=74.07 | 20.8x0.94 = 19.55 | 0.0005x0.94=0.00047 | 0.55 |

Although using Equation 4 (and subsequently Equation 5) overcomes the problems with dilution seen in Table 2, it does reintroduce the problems seen in Table1 where oxygen deficiencies are underestimated in cases where large oxygen deficiencies exist because of the increased measured nitrogen concentrations.

One of the advantages in persisting with referencing other tube bundle monitoring points for initial gas values is that any drift or systematic errors with the analysers are eliminated as they are common to both measurements.

**Airfree Calculations**

The use of airfree concentrations, particularly for carbon monoxide, is becoming more common. Airfree calculations must be used with caution. Airfree calculations have their origins in eliminating the effects on collected samples by dilution with air. The basis of the calculation is that all of the oxygen present is due to dilution of the gas of interest with air, i.e. no oxygen is present in the gas being sampled. This can be useful when taking samples from behind seals where samples collected are influenced by air leakage through the seal, as seen with barometric pressure changes. When monitoring a spontaneous combustion event sampling may be required at a frequency that does correspond to the seals "breathing out" (the time best suited to collecting a sample to indicate the composition of the goaf). As a result, the concentration of indicators gases such as carbon monoxide may actually fall between samples, giving the impression that any spontaneous combustion activity is diminishing. However, this reduction in concentration may be entirely due to the fact that the area being sampled has been diluted with air as the seal "breathed in". Airfree is extremely useful in these situations to eliminate the effect of the dilution.

Airfree calculations must be treated with caution when the sample collected is close to fresh air. When a sample is predominately air, you cannot calculate reliable airfree results: the sample is air and, therefore, cannot be air free. Small errors in measurement will be magnified in these cases. Airfree calculations don't take into account any oxygen that is present in the gas. If we have a gas mix that contains 18% oxygen and this gas reacts with coal in the goaf to produce carbon monoxide, the airfree carbon monoxide will be less than a reaction of the same intensity if the gas mix initially contains 20.9% oxygen.

Similarly if there is a significant spontaneous combustion event or fire in which substantial amounts of oxygen are being consumed by the oxidation reaction, airfree results will be under estimated. The lowered oxygen concentration is treated as less dilution and therefore a comparative lower airfree carbon monoxide concentration results. It is the same for samples collected from a heating in which there is a secondary mechanism for the loss of oxygen, such as when passing over broken coal left in the goaf. The oxygen is taken up by the coal but does not generate oxidation products (coal acts as an oxygen sponge). If this is the case, by the time the gas reaches the sample point, the oxygen has been reduced and therefore will result in a lower air free carbon monoxide concentration than if it was measured at the site of the heating.

To avoid problems in underestimating the intensity of an "event" without introducing the problems associated with airfree calculations, ratios of indicator gases and seam gases can be used or ratios of gases eluting higher up the fire ladder compared to those evolved at lower temperatures.

**Calibration Gases**

Regardless of how good the analytical equipment being used is, accuracy is influenced by the calibration gases used to set the response of the instrument. Calibration gas suppliers certify the composition of each component as the likely concentration with limits between which the true concentration lies.

**Table 4 Typical Calibration Gas Certification**

| Component | Concentration | Uncertainty | Concentration | Uncertainty | Concentration | Uncertainty |
|---|---|---|---|---|---|---|
| Hydrogen | 204ppm | ± 8ppm | 430ppm | ± 10ppm | 432ppm | ± 11ppm |
| Oxygen | 19.6% | ± 0.5% | 12.2% | ± 0.3% | 0.99% | ± 0.03% |
| Methane | 0.94% | ± 0.2% | 2.14% | ± 0.05% | 10.4% | ± 0.2% |
| Carbon Monoxide | 189ppm | ± 5ppm | 930ppm | ± 10ppm | 1550ppm | ± 400ppm |
| Carbon Dioxide | 0.98% | ± 0.2% | 1.95% | ± 0.05% | 12.4% | ± 0.3% |
| Ethylene | 114ppm | ± 4ppm | 190ppm | ± 10ppm | 104ppm | ± 3ppm |
| Ethane | 120ppm | ± 3ppm | 200ppm | ± 10ppm | 412ppm | ± 4ppm |

As can be seen in Table 4, some of the uncertainties are significant. If used to set the response of the instrument to what we think is 19.6% oxygen as indicated on the certificate, in reality it may be as low as 19.1% or as high as 20.1%. This will result in all oxygen measurements being slightly high or low, but analytically acceptable. This is common to all of the gases measured (according to their uncertainty). A change in calibration gas can lead to a step change in values measured by the sensor/instrument calibrated with that gas. Procedures should be in place to check calibration gases prior to using them for calibration. The influence that this uncertainty has on the interpretation of results can be significant, particularly for ratios incorporating oxygen deficiencies. The oxygen could easily be reading 0.2% high which will result in a much lower oxygen deficiency or could even result in what appears to be oxygen enrichment.

### Instrument Accuracy

When any analysis is performed there will always be slight inaccuracies in the measurements made, no matter how well the analysis was done and the how good the instrument performing the analysis is. These variations are totally acceptable and in fact expected. These slight variations from what may be the true concentration cause problems in samples with no significant oxygen deficiency whenever we get a slightly higher oxygen (or slightly lower nitrogen measurement by GC analysis), and apply the known fresh air ratio of oxygen to nitrogen to determine the oxygen deficiency. When this happens there will be issues (mathematically) in determining Graham's Ratio (and any other ratios using oxygen deficiency). It appears that we have actually created oxygen, which goes against all that is known about the reactions of oxygen in the underground coal mining environment. What it really indicates is that the ratio has stayed the same. We have neither used nor created oxygen and that the difference comes totally from the acceptable inaccuracies (tolerance) of the measurement technique. As mentioned previously, this is why it is not recommended to use such ratios and calculations when the samples are so close to air or show no signs of oxygen deficiency.

AS2290.3 outlines the requirements for acceptable tolerances for underground gas monitoring equipment.
The allowed percent relative error in reading (%RE) = 10-%FS/20
and % FS = percentage of full scale concentration.
The maximum error (ME) =TCx%RE/100
Where TC = True gas concentration.
The output produced shall be within TC ± ME
This applies for all sensors except oxygen, for which a tolerance of ± 0.2% is applied to all concentrations above 15%. Typical responses for gases of known concentration applied immediately following calibration are displayed in Tables 5 and 6. All of these responses are within the tolerances of AS2290.3.

**Table 5 Infrared and Oxygen Paramagnetic Analyser Responses**

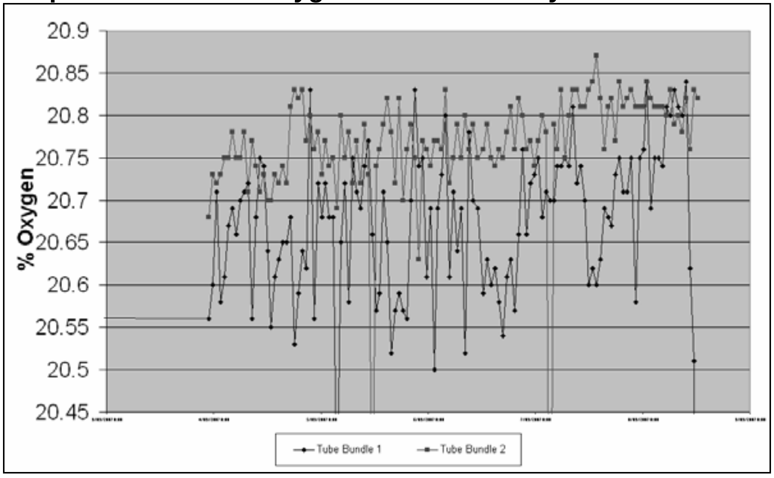
| Oxygen | | Methane | | Carbon Monoxide | | Carbon Dioxide | |
|---|---|---|---|---|---|---|---|
| **True Conc.** | **Measured Conc.** | **True Conc.** | **Measured Conc.** | **True Conc.** | **Measured Conc.** | **True Conc.** | **Measured Conc.** |
| 18.9% | 18.9% | 90.0% | 90.4% | 900ppm | 906ppm | 90.0% | 88.2% |
| 15.8% | 15.9% | 75.0% | 75.1% | 750ppm | 751ppm | 75.0% | 73.9% |
| 12.6% | 12.7% | 60.0% | 58.8% | 600ppm | 607ppm | 60.0% | 59.6% |
| 9.5% | 9.6% | 45.0% | 44.3% | 450ppm | 444ppm | 45.0% | 44.8% |
| 6.3% | 6.5% | 30.0% | 29.1% | 300ppm | 291ppm | 30.0% | 30.1% |
| 3.2% | 3.3% | 15.0% | 14.2% | 150ppm | 146ppm | 15.0% | 15.0% |

**Table 6 Electrochemical/Pellistor Analyser Responses**

| Oxygen | | Methane | | Carbon Monoxide | |
|---|---|---|---|---|---|
| **True Conc.** | **Measured Conc.** | **True Conc.** | **Measured Conc.** | **True Conc.** | **Measured Conc.** |
| 20.9% | 20.9% | 4.0% | 3.98% | 100ppm | 96ppm |
| 18.1% | 18.2% | 3.0% | 2.92% | 50ppm | 47ppm |
| 15.2% | 15.0% | 1.0% | 0.92% | 25ppm | 23ppm |
| 11.1% | 11.0% | | | | |

## Instrument Variations

**Graph 10 Fresh Air Oxygen as Measured by Tube Bundle**



Graph 10 indicates the variation in the measurement of oxygen using the tube bundle. The points plotted are from two different tube bundle systems sampling fresh air on the surface. We can assume that the fresh air concentration of oxygen at these locations remains relatively stable and that the variations seen are as a result of the instrument measuring the concentration. The graph shows that the variations between the two systems are different, with one often returning changes of 0.1% between samples. Although the other system did return some differences of this magnitude, most were of the order of 0.05% or less. Variations of this magnitude can significantly influence any trending of ratios that incorporate an oxygen deficiency, as the calculated oxygen deficiencies can halve or double between readings. Graph 10 was for tube bundle data only, as no real time oxygen data from the surface was available. However, inference from Graph 1 Real Time vs Tube Bundle $O_2$ Data, would imply that the variation in oxygen measurements using real time sensors would make the problems with oxygen deficiency ratios worse. When the oxygen being measured is close to fresh air, even the resolution of the instrument can affect these calculations.

## Analysis for Flammability Assessment

The need to perform a complete analysis by GC of atmospheres generated during coal fires or heatings is not only critical but the only option to obtain an accurate assessment of the flammability status of the underground environment.

Failure to do so can lead to wrongly assessing the atmosphere to be inert, when in fact it could be explosive or fuel rich, due to the generation of percent levels of carbon monoxide and hydrogen during mine fires. The presence of percent levels of these gases not only adds to the percentage of combustible gases present but also has a major influence in the lowering of the oxygen nose point (the lowest oxygen concentration at which an explosion can occur).

Figures 1 to 6 are examples of explosibility diagrams generated by GC analysis and tube bundle analysis of the same gas mix coming from heatings and mine fires. Because the tube bundle analysis does not include the hydrogen, and only includes up to 1000ppm carbon monoxide, the percentage of combustible gas is underestimated and the calculation of the combustible (explosive) zone is incorrect. In a fire or heating situation, without the GC analysis an assessment of the flammability of the atmosphere underground is likely to be unreliable and can indicate that the atmosphere is inert when in reality it is explosive.

**Fig. 1 Explosibility determined by Tube Bundle**

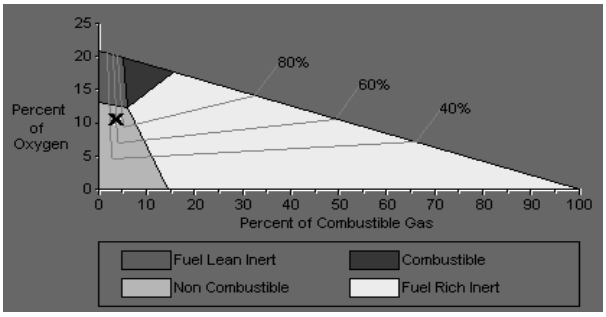
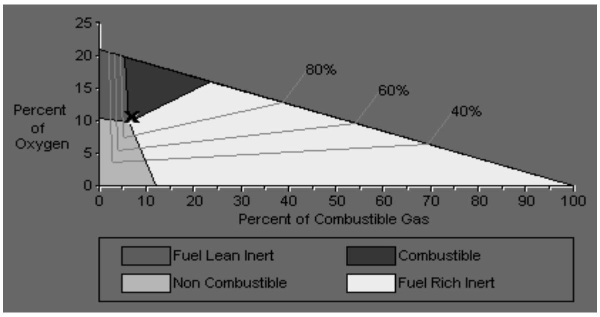


**Fig. 2 Explosibility determined by GC**



Gas Mix; 1.26%$H_2$, 10.45%$O_2$, 78.85%$N_2$, 3.93%$CH_4$, 1.82%CO, 3.66%$CO_2$, 130ppm$C_2H_4$, 179ppm$C_2H_6$

**Fig. 3 Explosibility determined by Tube Bundle**

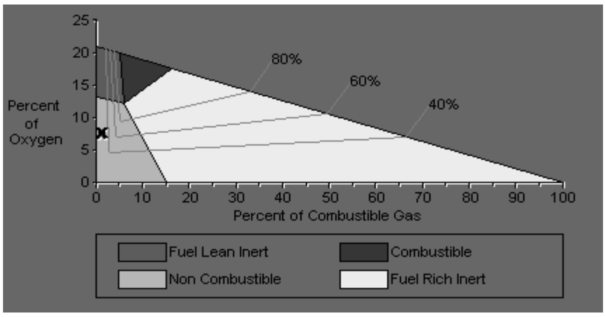
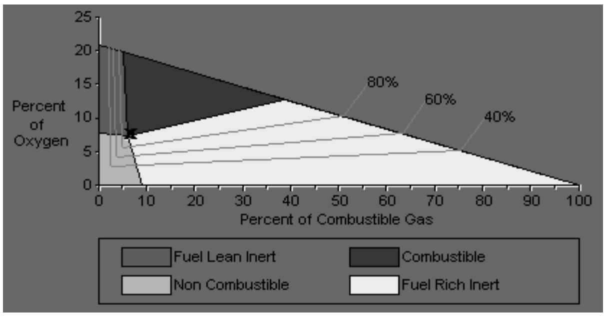


**Fig. 4 Explosibility determined by GC**



Gas Mix; 2.90%$H_2$, 7.51%$O_2$, 78.45%$N_2$, 1.38%$CH_4$, 2.02%CO, 6.67%$CO_2$, 480ppm$C_2H_4$, 1082ppm$C_2H_6$

**Fig. 5 Explosibility determined by Tube Bundle**

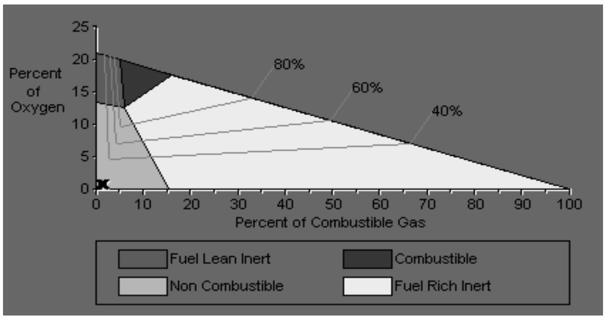
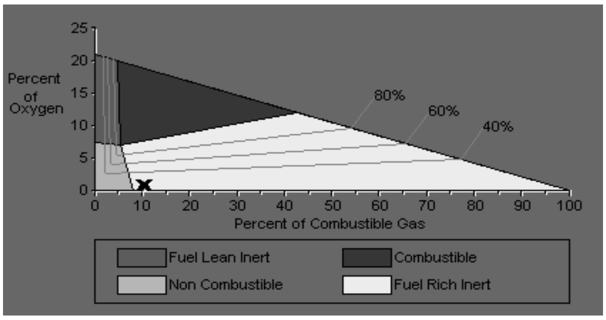


**Fig.6 Explosibility determined by GC**



Gas Mix; 6.48%$H_2$, 6.48%$O_2$, 73.17%$N_2$, 1.99%$CH_4$, 2.33%CO, 15.07%$CO_2$, 1152ppm$C_2H_4$, 774ppm$C_2H_6$

## Conclusions

- An effective gas monitoring system includes real time sensors, a tube bundle system and a gas chromatograph. Each technique has strengths and weaknesses which must be known by those both operating them and using the generated results for interpretation.
- Anyone interpreting data must be aware of any limitations and implications of the indicators being used.
- Care must be taken when calculating oxygen deficiencies to ensure that the calculation is correct and representative for the sample and analysis technique.
- Ratios including Graham's Ratio that incorporate oxygen deficiency can be unreliable for samples where oxygen deficiencies are less than 0.3%.
- Airfree calculations are effective for removing the influence dilution with air has on the sample, but calculations from samples consisting of mostly air must be used with caution as any errors in measurement of remaining gases are magnified. Calculations may not be reliable when the oxygen present has not come from dilution of the sample of interest but is part of that gas mix.
- Interpretation of data is best done looking at trends rather than one off samples. Even if the ratio is being underestimated, any increase in intensity should result in an increase in the trend although the rate of change may not match the increase in intensity.
- Trends should only be based on data collected from the same technique using the same format for calculations.
- When any analysis is performed there will always be slight inaccuracies in the measurements made, no matter how well the analysis was done and the how good the instrument performing the analysis is. These variations are totally acceptable and in fact expected.

- A true indication of the flammability of the mine atmosphere during a mine fire, heating or post explosion can only be determined by gas chromatograph analysis due to the high concentrations of carbon monoxide and hydrogen possible.

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