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PROBLEMS WITH DETERMINING OXYGEN DEFICIENCIES IN RATIOS USED FOR ASSESSING SPONTANEOUS COMBUSTION ACTIVITY

Darren Brady¹

ABSTRACT: Several common ratios used for determining spontaneous combustion activity rely on comparing the amount of particular products of oxidation with the amount of oxygen consumed to produce these products. Oxidation reactions become more efficient as the coal gets hotter, meaning more products produced for less oxygen consumed. There are many problems associated with accurately determining the true amount of oxygen used for use in these ratios. These problems relate to the monitoring technique (and its associated uncertainties) used to generate the results, deficiencies in the established equations utilised in calculations, dilution with other gases and other sources of oxygen depletion. Typically the oxygen deficiency is over estimated, resulting in the under estimation of the indicating ratio. For this reason the use of "one off" calculations to determine the status of the underground environment is not recommended. Instead trends of these ratios should be used to identify increases which indicate an increase in oxidation intensity. This paper outlines problems associated with the monitoring techniques and equations used to determine the oxygen deficiency.

INTRODUCTION

Oxygen deficiency is a term used for the amount of oxygen used (consumed/removed) from the inlet air stream by any activity as it undergoes reactions and interactions with the coal. Ratios utilising oxygen deficiency have been in use since at least 1921 (Cliff, Rowlands, Sleeman 1996) and are still valued tools in the identification and assessment of spontaneous combustion. In fact it is a requirement under Queensland's mining legislation for mines to detect and calculate Graham's ratio at certain locations. These ratios are used to measure the intensity of any oxidation of the coal that may be occurring. As the coal gets hotter the oxidation reaction becomes more efficient and more oxygen is converted to products of oxidation, such as carbon monoxide and carbon dioxide. Ratios such as Graham's, Young's and Jones-Trickett's all divide products of combustion by the amount of oxygen consumed to give a quantifiable measure of how much oxygen was used to generate the amount of combustion products measured.

If there is more than one source of oxygen depletion than these ratios will be under estimated as it appears that more oxygen was used to produce the products than was really the case.

The measurement technique and the actual equation used for calculating the oxygen consumed by any oxidation/absorption-adsorption process also have a significant influence on the calculated values for these ratios. It is essential that anyone using these ratios to assess the status of the underground environment, understands the limitations and implications of both the analytical techniques and equations used to measure/determine the oxygen consumed. Graham's ratio will be used to demonstrate these limitations and implications however it should be noted that the same are applicable to any ratio incorporating oxygen deficiency.

CALCULATING OXYGEN DEFICIENCY

Common Equations

Graham's ratio is often expressed as

$$GR = \frac{100 \times CO_f}{0.265 \times N_{2f} - O_{2f}} \quad (1)$$

Where:

GR = Graham's ratio

CO_f = final carbon monoxide concentration (%)

N_{2f} = final nitrogen concentration (%)

O_{2f} = final oxygen concentration (%)

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This format of the equation enables calculation of a result without actually knowing what the initial gas concentrations were. The denominator in Equation 1 represents the oxygen deficiency and is based on the assumption that nitrogen, being an inert gas, will not be consumed or 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 equation 2 can be used to calculate the initial oxygen concentration by using the amount of nitrogen determined to be present in the sample;

$$O_{2i} = 0.265 \times N_{2f} \quad (2)$$

Where:

O_{2i} = initial oxygen concentration (%)

N_{2f} = final nitrogen concentration (%)

The measured oxygen concentration in the sample is then subtracted from the calculated initial oxygen to give the oxygen deficiency as in Equation 3.

$$OD = 0.265 \times N_{2f} - O_{2f} \quad (3)$$

Where:

OD = oxygen deficiency (%)

N_{2f} = final nitrogen concentration (%)

O_{2f} = final oxygen concentration (%)

The use of the fresh air nitrogen concentration of 79.02% includes argon (Ar) 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 will also be diluted.

Equation 3 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 nothing replaces it, although the actual number of nitrogen molecules does not increase, the percentage of the gas that is nitrogen does. This is often the case in a goaf where coal is left behind and oxygen is absorbed and adsorbed by the coal without producing oxides of carbon. This causes problems with the calculation of the oxygen deficiency, because of the elevated nitrogen concentration the calculated initial oxygen concentration is over estimated and therefore so is the oxygen deficiency. This is typical for samples collected from sealed or non ventilated areas. Examples from real mine samples highlighting this are outlined in Table 1.

Table 1 shows that when using Equation 2 in cases where significant oxygen deficiencies exist, the calculated initial oxygen can be greater than that in fresh air (20.95 %), an obvious problem. This over estimation of initial oxygen, results in an increased calculated oxygen deficiency which in turn leads to an under estimation of ratios using oxygen deficiency as the denominator. This is because it appears that more oxygen was used in the reaction and therefore was less efficient than is really the case.

Equation 1 is suited to situations where the initial gas concentrations are not available. With these ratios we are looking at how the gas concentrations have changed as they pass through an area. If initial gas results are available Graham's ratio is often calculated using;

$$GR = \frac{100(CO_f - CO_i)}{O_{2i} - O_{2f}} \quad (4)$$

Where:

GR = Graham's ratio

CO_f = final carbon monoxide concentration (%)

CO_i = initial carbon monoxide concentration (%)

O_{2i} = initial oxygen concentration (%)

O_{2f} = final oxygen concentration (%)

This equation is frequently used by mines that include a sampling point in an intake in its tube bundle gas monitoring system. Any problems associated with the calibration or drift of the oxygen analyzer are negated when

using this equation as they are common to both measurements. However 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

Table 1 - Oxygen deficiency calculations				
O ₂ (%)	N ₂ (+ Ar) (%)	Initial O ₂ (%)	OD(%) Eq 3	Initial O ₂ * (%)
2.3	81.8	21.7	19.4	18.65
9.2	80.4	21.3	12.1	11.75
15.7	83.1	22.0	6.3	5.25
8.1	89.1	23.6	15.5	12.85

*calculated
assuming
initial
oxygen
20.95%.

Table 2 - Graham's ratio calculations using Equation 4				
CH ₄ (%)	O _{2i} (%)	O _{2f} (%)	CO _f (%)	GR
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

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%) and the initial carbon monoxide taken as 0 %.

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. In this case dilution only, has led to a decrease in Graham's ratio by a factor of ten. To overcome this problem the oxygen deficiency is best calculated as;

$$OD = \left(\frac{N_{2f}}{N_{2i}} \right) \times O_{2i} - O_{2f} \tag{5}$$

Where:

- OD = oxygen deficiency (%)
- N_{2f} = final nitrogen concentration (%)
- N_{2i} = initial nitrogen concentration (%)
- O_{2i} = initial oxygen concentration (%)
- O_{2f} = final oxygen concentration (%)

Multiplying the initial oxygen by the ratio of the final and initial nitrogen in Equation 5 takes into account any dilution and overcomes the problems demonstrated with Equation 4 as the nitrogen will have also been diluted. The same factor is applied to the initial carbon monoxide to give the equation;

$$GR = \frac{100 \times \left(CO_f - CO_i \frac{N_{2f}}{N_{2i}} \right)}{\left(O_{2i} \times \frac{N_{2f}}{N_{2i}} \right) - O_{2f}} \tag{6}$$

Where:

GR = Graham's ratio

CO_f = final carbon monoxide concentration (%)

CO_i = initial carbon monoxide concentration (%)

N_{2f} = final nitrogen concentration (%)

N_{2i} = initial nitrogen concentration (%)

O_{2i} = initial oxygen concentration (%)

O_{2f} = final oxygen concentration (%)

Table 3 shows how Equation 6 overcomes problems seen with Equation 4 caused by dilution when using initial oxygen concentrations. Initial concentrations of 20.95% oxygen, 79.02% nitrogen and 0ppm carbon monoxide have been used.

Although using Equation 5 (and subsequently Equation 6) overcomes the problems with dilution seen in Table 2, it does reintroduce the problems seen in Table 1 where oxygen deficiencies are underestimated in cases where large oxygen deficiencies exist because of the increased measured nitrogen concentrations. The advantage in persisting with referencing other tube bundle monitoring points for initial gas values is that any drift or systematic errors with the analyzers are eliminated as they are common to both measurements.

Table 3 - Graham's ratio calculations using Equation 6

CH ₄ (%)	N _{2f} (%)	O _{2f} (%)	CO _f (%)	GR
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

The Influence of Analytical Techniques

Neither tube bundle nor real time systems measure nitrogen. To calculate oxygen deficiency using any of the equations that require 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 analyzers used in mining are required to meet tolerances of +/- 0.2 % (according to Australian Standard 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 % CO₂ and 20.7 % O₂, 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 Equation 1
Graham's Ratio could range between:

$$\begin{aligned} GR &= 100 \times 0.001 / (0.265 \times 79.4 - 20.5) \\ &= 0.1 / (21.04 - 20.5) \\ &= 0.1 / 0.54 \\ &= 0.18 \text{ and} \end{aligned}$$

$$\begin{aligned} GR &= 0.001 \times 100 / (0.265 \times 79.0 - 20.9) \\ &= 0.1 / (20.94 - 20.9) \\ &= 0.1 / 0.04 \\ &= 2.86 \end{aligned}$$

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).

Oxygen measurements made using paramagnetic analysers tend to return much more stable results than those measured using electrochemical sensors employed in real time monitoring systems as can be seen in Figure 1.

Figure 1 compares measurements made at the same underground monitoring location using real time sensors and an oxygen paramagnetic analyzer employed in a tube bundle system. It highlights that oxygen measurements are much more stable using the tube bundle than for the real time sensor which regularly varied by more than 0.3 % (absolute) between measurements. Variations of the magnitude seen with the real time sensors have a significant impact on calculated oxygen deficiencies and subsequent ratios.

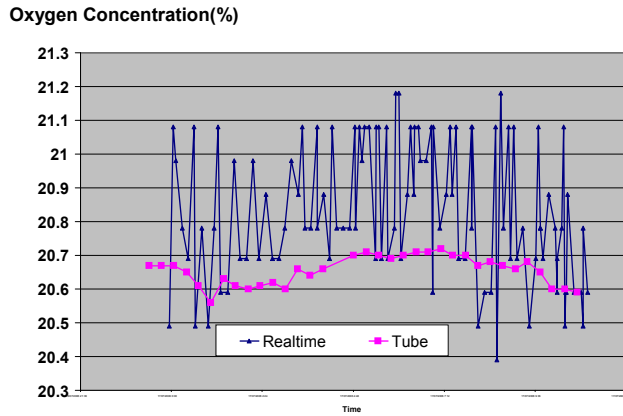


Figure 1 - Real time vs tube bundle oxygen measurements

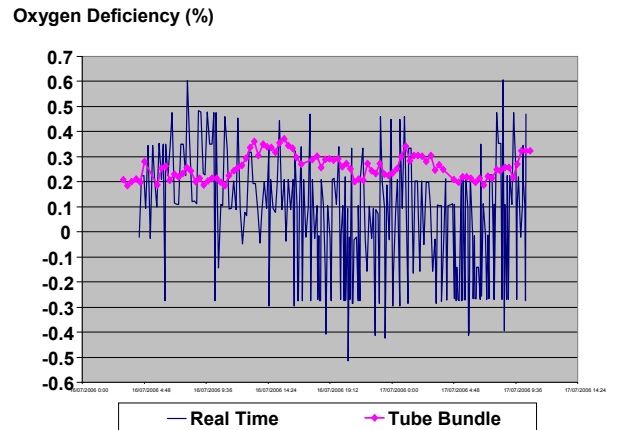


Figure 2 - Real time vs tube bundle oxygen deficiencies

Figure 2 compares oxygen deficiencies calculated using Equation 3 for measurements made in a longwall return using real time and tube bundle data. The data shows that the tube bundle again returns the more stable data with the real time data frequently returning negative oxygen deficiencies, indicating the highly unlikely production, rather than consumption of oxygen.

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 seen in Figures 1 and 2, the variation in oxygen concentration using real time monitoring results in problems with calculating the oxygen deficiency that essentially make this monitoring technique unsuited to the calculation of Graham's ratio in these locations.

Although the tube bundle appears much more stable it must be remembered 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. This variation will obviously affect the reliable determination of oxygen deficiencies and hence indicating ratios.

Gas chromatography (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, Equations 1, 2 and 3 must be modified if the results determine argon separate to nitrogen. All these equations 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, the fresh air ratio is 20.95 % oxygen to 78.1 % nitrogen (20.95/78.1=0.268). Equation 1 should be modified to:

$$GR = \frac{100 \times CO_f}{0.268 \times N_{2f} - O_{2f}} \tag{7}$$

Equation 2 modified to:

$$O_{2i} = 0.268 \times N_{2f} \tag{8}$$

And similarly Equation 3 modified to:

$$OD = 0.268 \times N_{2f} - O_{2f} \tag{9}$$

If this is not taken into account, oxygen deficiencies and subsequent indicating ratios will be incorrect and in fact 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.

Minimum Oxygen Deficiency Required

Mitchell (1996) states that Graham's 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."

The calculated oxygen deficiencies for a typical longwall return in Figure 2 show the majority are less than the recommended minimum of 0.3% meaning use of ratios incorporating oxygen deficiency must be used with caution.

This problem associated with calculating Graham's ratio when only small oxygen deficiencies exist also has implications for the requirement in Part 7 of Queensland's "The Coal Mining Safety and Health Regulation (2001)" to automatically detect and calculate the value of carbon monoxide to oxygen deficiency (Graham's ratio). When oxygen deficiencies are less than 0.3% (often the case in a longwall return) the variation and resolution of the measuring device contribute significantly to the calculated ratio.

Influence of Instrument Inaccuracies

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 oxygen has actually been created, 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. Table 4 demonstrates this with results from GC analysis for samples collected in a longwall tailgate. Because analysis was by GC and nitrogen and argon reported separately Equation 9 is used to calculate oxygen deficiency.

Table 4 - Calculated oxygen deficiencies			Figure 3 - Fresh air oxygen as measured by tube bundle
O ₂ (%)	N ₂ (%)	Oxygen Deficiency (%)	
20.61	76.63	-0.07	
20.57	76.73	-0.01	
20.33	75.84	0.00	
20.23	75.71	0.06	

Table 5 shows that some samples return a negative oxygen deficiency which will result in a negative value for any ratios using oxygen deficiency. It is often assumed that this means that there is a problem with the analysis, as it is impossible to create oxygen underground. A closer look at the results will explain what is happening.

In the first sample the nitrogen was measured to be 76.63 % and a negative oxygen deficiency obtained. If a result of 76.91 % had been returned the oxygen deficiency would have been positive. This represents a difference of 0.28 % (absolute) or 0.37 % (relative). This magnitude of variation is well within the tolerance expected for this analysis.

Similarly take the oxygen concentration measured as 20.61 % in the first sample, if in fact it had been measured as 20.53 % the oxygen deficiency would have been positive. This represents a difference of 0.08 % (absolute) or 0.39 % (relative). This is again, well within the tolerance expected for this analysis.

We can go even further and look at an even smaller decrease in the oxygen in combination with an increase in the nitrogen. For example if the oxygen came back as 20.57 % and the nitrogen 76.77 % (only very small changes) we would get a positive oxygen deficiency.

This is not peculiar to this sample but could be applied to all samples in the above table that returned negative excess nitrogen values. In general decreases in oxygen of less than 0.1 % or increases in nitrogen of approximately 0.2% will result in all samples with a negative oxygen deficiency becoming positive.

This just highlights that when we are analysing samples in which the oxygen to nitrogen ratio has remained constant, small, but expected analytical errors create problems ratio calculations that include oxygen deficiencies. This is why these ratios calculations are not suitable for these types of samples.

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. For example, the reported oxygen concentration in a recently supplied certified calibration gas is 19.6 ± 0.5 %.

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 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 Variation

Figure 3 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. Figure 3 was for tube bundle data only, as no real time oxygen data from the surface was available. However, inference from Figure 1 Real time vs tube bundle oxygen 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 adversely affect these calculations.

SUMMARY AND CONCLUSION

Despite the problems highlighted in the text of this paper ratios incorporating oxygen deficiencies can still be very useful in the identification of the onset of spontaneous combustion or as an indicator of intensity during a spontaneous combustion event. Those involved in the interpretation must however be aware of all of these implications.

- 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 %.
- Ratios incorporating oxygen deficiency will underestimate if there is more than one source of oxygen deficiency.
- Due to the variation in measurement and the small oxygen deficiencies present, real time monitoring is not suited to determining Graham's ratio in longwall returns.
- 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.
- 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.

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