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REVIEW OF OXYGEN DEFICIENCY REQUIREMENTS FOR GRAHAM'S RATIO

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ABSTRACT: Graham's ratio is a commonly used indicator for measuring the intensity of the oxidation of coal in underground mine atmospheres. Successful measurement of oxygen deficiency is critical in order to generate relevant results, as well as meaningful data trends. Graham's ratio is often used as a trigger for Trigger Action Response Plans (TARP) for the management of spontaneous combustion.

If a Graham's ratio is calculated where there is an insufficient oxygen deficiency the result can be overestimated and trigger a TARP level. Mitchell (1996) and the NSW Mines Rescue gas detection and emergency preparedness book (2014) has previously identified issues with using Graham's Ratio when the oxygen deficiency is less than 0.3%, due to analytical limitations. This issue is often encountered in samples in which the composition is close to air due to the low inherent oxygen deficiency of the sample. The same problem is identified in samples diluted with seam gas. Errors in oxygen deficiency can be compounded by inaccuracies in other measured components when nitrogen is calculated by difference.

A concern with applying the 0.3% oxygen deficiency requirement (minimum limit) to dilute or close to air samples is that valid data may be excluded from interpretation. This paper will review the magnitude and application of minimum oxygen deficiency required for a consistent valid measurement of Graham's ratio. This will be done across a range of samples using real data from a number of modern analysis techniques in underground coal mines.

INTRODUCTION

Graham's ratio is a commonly used gas ratio in the analysis of underground coal mine atmospheres. It is a measure of the efficiency of conversion of oxygen to carbon monoxide. It is also a significant tool in the ability to predict the onset of a heating or the intensity of a heating (Cliff, *et al.*, 2004).

Raw carbon monoxide concentrations are not always indicative of the intensity of a heating due to dilutions or accumulation of gases. By comparing carbon monoxide generated to oxygen deficiency a more relative measurement can be made (Graham's ratio). This measurement is independent of air flow and various forms of the equation account for dilution effects (Cliff, *et al*., 1999).

The State of Queensland requires continuous gas monitoring and calculation of Graham's ratio in the return for every ventilation split (State of Queensland, 2001). Graham's ratio is often used as a trigger in a coal mines spontaneous combustion Trigger Action Response Plan (TARP) for active longwalls and sealed goafs.

TARP Action levels based on overseas experience are usually set as (Cliff, *et al*., 2004):

- < 0.4% Normal
- 0.4% to 1.0% Investigate
- 1.0% Heating
- 2.0% Serious Heating / Fire

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However these trigger values may be too high for Australian coal mines (Cliff, *et al*., 1999) and the following alternative trigger values have been suggested for Australian mines (NSW Mines Rescue, 2014):

- < 0.1%: Normal
- 0.2% to 0.3% Investigate
- 0.4% to 0.7% Heating

Graham's ratio can effectively be simplified to the following equation:

Equation 1:

$$Graham's\ Ratio = \frac{100 \times carbon\ monoxide\ produced\ (\%)}{oxygen\ deficiency\ (\%)}$$

In order to determine both the carbon monoxide produced and the oxygen deficiency the initial gas readings are essential. The equation 1 is thus expanded to the following form:

Equation 2:

$$Graham's\ Ratio = \frac{100 \times \left(carbon\ monoxide_{final} - carbon\ monoxide_{initial}\right)}{oxygen_{initial} - oxygen_{final}}$$

Measurement of the initial carbon monoxide and also the initial oxygen can be done in several different ways. This is mostly dependant on what information is available. If no initial readings are available, fresh air is typically assumed as the initial readings (Cliff, *et al*., 2004).

The effects of dilution must also be taken into account. When assuming fresh air as the initial gas state, the final nitrogen reading can be used to calculate the initial oxygen result (Cliff, *et al*., 2004).

Therefore when using an analytical technique that measures nitrogen by difference, the following common form of the equation is derived:

Equation 3:

$$Graham's\ Ratio = \frac{100 \times \left(carbon\ monoxide_{final}\right)}{\left(0.265 \times nitrogen_{final}\right) - oxygen_{final}}$$

Note that the constant 0.265 is simply the theoretical ratio of oxygen to nitrogen in air. Equation 3 is commonly used to calculate Graham's ratio on real time sensors underground.

Using a measured fresh air value and taking dilution into account is represented by the Equation 4:

Equation 4:

$$Graham's\ Ratio = \frac{100 \times \left(carbon\ monoxide_{final} * \frac{nitrogen_{final}}{nitrogen_{initial}}\right) - carbon\ monoxide_{initial}}{\left(oxygen_{initial} \times \frac{nitrogen_{final}}{nitrogen_{initial}}\right) - oxygen_{final}}$$

Equation 4 is a common equation used to calculate Graham's ratio for tube bundle monitoring points in underground coal mines. The measured fresh air point is typically from a point on the surface at the tube bundle building, or from an intake roadway underground.

LIMITATIONS DUE TO OXYGEN DEFICIENCY

An oxygen deficiency needs to be present for the Graham's ratio to be calculated. It is impossible for oxygen to be created or generated underground; as such the final oxygen can never exceed the initial oxygen. However, due to the analytical error of analysers and the tolerance for oxygen monitors being ± 0.2% (Council of Standards Australia, 1990), it is not uncommon for higher final oxygen to be measured relative to the theoretical or measured initial oxygen, even though only a small oxygen deficiency exists. The analyser analytical error is considered normal and expected (Brady, 2007). The example below shows Graham's ratio calculation using a real time sensor gas reading and equation 3:

Table 1: Real time sensor gas reading

Gas	Percentage (%)
Oxygen	20.9
Methane	0.5
Carbon dioxide	0.3
Carbon monoxide	0.01
Nitrogen (by difference)	78.3

$$Graham's\ Ratio = \frac{100 \times (carbon\ monoxide_{final})}{(0.265 \times nitrogen_{final}) - oxygen_{final}}$$

$$Graham's\ Ratio = \frac{100 \times (0.0001)}{(0.265 \times 78.3) - 20.9}$$

$$Graham's\ Ratio = \frac{0.01}{-0.15}$$

$$Graham's\ Ratio = -0.06$$

The negative oxygen deficiency result gives a negative Graham's ratio, which is theoretically impossible and the Graham's ratio result is unusable. A negative Graham's ratio result is an invalid result which cannot be used for interpretation. Real time sensors in return airways often exhibit negative or non-realistic readings of this nature. Figure 1 shows an example of Graham's ratio being calculated from real time sensors in a return airway location with a small oxygen deficiency.

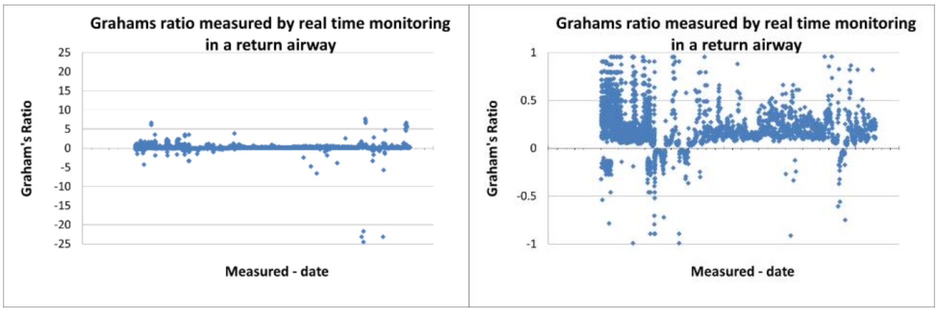

Figure 1: Real time sensor Graham's ratio in return airway location (same data, different y-axis scales)

Figure 1 clearly shows that this Graham's ratio trend is unreliable. Values range from in the negative to in excess of 0.4 which would indicate a heating or fire. This location had a low and constant carbon monoxide reading, thus it is apparent that the fluctuation in Graham's ratio is mostly due to the oxygen deficiency.

It has been reported that any oxygen deficiency less than 0.2% should be treated with caution due to the possibility of analytical error (NSW Mines Rescue, 2014). Brady (2007) has stated that Graham's ratio can be unreliable for oxygen deficiencies below 0.3%.

By limiting Graham's ratio calculations to an oxygen deficiency of at least 0.3%, which exceeds the allowable error of oxygen sensors in underground coal mines (Council of Standards Australia, 1990), it is far more likely to calculate reliable Graham's ratio. This oxygen deficiency requirement of 0.3% minimum is commonly used as a threshold for the Graham's ratio calculation. Automated monitoring systems are often programmed to remove any readings which don't meet this oxygen deficiency requirement. This eliminates potential unreliable ratio calculations which could contribute to alarm fatigue.

Figure 2 shows the result of Graham's ratio when the oxygen deficiency requirements were applied. The dataset used is the same dataset used in Figure 1.

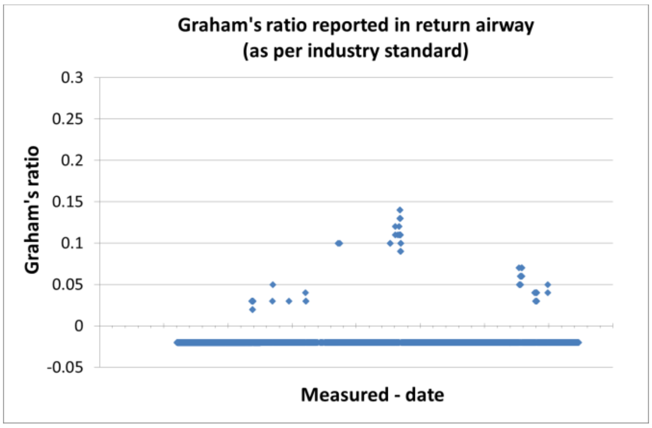

Figure 2: Graham's ratio with oxygen deficiency ≥ of 0.3% oxygen

Note that in Figure 2 most of the Graham ratio results have been eliminated and the data produced is not helpful in generating a trend. This occurrence is frequent for any real time monitoring points with gas atmospheres of low oxygen deficiencies. Brady (2008) concludes: "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."

Although the occurrence of unreliable Graham's ratio calculations is most prevalent on real-time systems for airway monitoring, it is also possible for tube bundle readings. This is particularly relevant for goaf samples heavily diluted with seam gases with a low oxygen deficiency. This scenario could arise by unintentional air ingress into a sealed area. Because Graham's ratio needs to take dilution into account, errors in nitrogen calculated by difference will result in an error in initial oxygen. Small cumulative errors in other major components thus have an effect on calculated initial oxygen. Gas chromatograph analysis can also experience errors in oxygen to nitrogen ratio due to analytical factors (Brady, 2007). This problem with insufficient oxygen deficiencies due to analytical error exists in all gas analysis techniques.

Current practice

Currently a common practice in automated monitoring systems generating a Graham's ratio is to apply the 0.3% oxygen deficiency requirement to the theoretical oxygen value which will filter out any readings close to air. This eliminates a majority of unreliable data generated in main and return airways. However at the same time this process will indiscriminately filter out useful valid data.

Measurements made with an oxygen deficiency of less than 0.3% may still be reliable in some situations and generate critical data for underground air monitoring.

Unreliable data and false triggers still occur in samples diluted with seam gas because the oxygen is reduced without a significant oxygen deficiency due to dilution. The current practice of basing the oxygen deficiency requirement upon the initial oxygen reading does not help to eliminate unreliable data in samples diluted with seam gas.

METHODOLOGY

Determination of values suitable for testing:

It is believed that the following conditions need to be met for an optimal oxygen deficiency to be determined:

- optimal reduction in unreliable data (avoid alarm fatigue)
- minimal loss of valid data
- increase overall utilisation of Graham's ratio trend and triggers by improving the generation of meaningful data

Two Graham's ratios are presented in Figure 3. One was calculated using a constant carbon monoxide value against an incrementally decreasing oxygen deficiency (triangle) and the second utilizing increasing CO values (diamond).

Figure 3 shows that with both a static or variable carbon monoxide value and an incrementally decreasing oxygen deficiency the trend appears to be linear until around 0.3% oxygen deficiency. Oxygen deficiencies, smaller than 0.05%, give an exponential increases in Graham's ratio with each increment. By inspecting the rate of change for Graham's ratio it is apparent that any Graham's ratio with a corresponding oxygen deficiency below 0.05% will exhibit variability with every increment of oxygen deficiency that it is unusable and thus considered unreliable or invalid. Further observations of Graham's ratio show that, regardless of the magnitude of the carbon monoxide reading, the rate of change of the Graham's ratio trend remains unchanged with decreasing oxygen deficiency as shown in Figure 3.

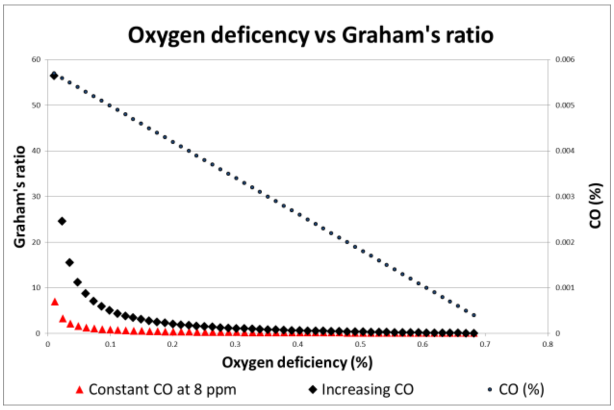

Figure 3: Oxygen Deficiency against Graham's ratio at a constant CO value (8 ppm) and variable CO

Considering the observed rate of change, the following minimum oxygen deficiency values were used for testing:

- 0.05% – This value appears to be the lowest and most conservative value, as all lower oxygen deficiencies are excessive compared to the previous trend.

- 0.1% - This value was selected as a more conservative value, considering data retention as a key requirement.
- 0.3% - This is the current literature value; it is the minimum oxygen value to be considered to avoid potential alarm fatigue.

Data collection and processing:

Data in the form of tube bundle and real time monitor logs were obtained from gas monitoring software. These logs were obtained, with permission, from three underground coal mines in Australia, all of which had previously experienced and flagged invalid Graham's ratio triggers in their alarm logs. The locations containing low oxygen deficiencies (around 0.5 or less) were chosen for the study. Each relevant data log was extracted to a Comma Separated Values (CSV) file containing the following information:

- Date and time of measurement
- Monitoring point number (location)
- Methane concentration (%)
- Carbon Monoxide concentration (%)
- Oxygen concentration (%)
- Carbon Dioxide concentration (%)
- Carbon Monoxide Make (Litres per minute)
- Graham's ratio - calculated.

These measured gas components are common to all tube bundle and real time analysis used in the testing. Nitrogen is determined by difference in all cases, as the sum of all measured components subtracted from 100%. These default gas components are sufficient to calculate a theoretical Graham's ratio based on theoretical air for the initial values.

In addition to these gas components, the Graham's ratio calculated from the gas monitoring software, as per industry standards, was extracted with each set of gas readings. The CO make value correlating with each data measurement was also extracted where possible.

These extracted data logs were processed in order to calculate a theoretical oxygen deficiency and theoretical Graham's ratio values based on fresh air as the initial readings.

For several tube bundle locations the measured initial air values were used rather than the theoretical initial values. This allowed the Graham's ratio calculation to be replicated as accurately as possible, reproducing the actual values calculated by the mine site monitoring system before extraction. This was not practical to do for all tube bundle locations due to limitations in data processing. Locations processed in this regard were compared to locations processed using theoretical air values, as a means to validate extrapolation of the theoretical data. Real time Graham's ratio was only calculated using theoretical air. The calculated Graham's ratio value for each measurement was categorised based on the following thresholds:

- Normal data was defined as any data with corresponding theoretical Graham's ratio calculated at 0.2 or below. This range is often used as normal conditions for spontaneous combustion management TARPs in Queensland mines (NSW Mines Rescue, 2014).
- Investigate data is defined in this testing as any data with theoretical Graham's ratio calculated at 0.2 to 0.4. This range is often used as an 'investigate' trigger for spontaneous combustion management TARPs in Queensland mines (NSW Mines Rescue, 2014).
- An invalid trigger is defined as any data with theoretical Graham's ratio calculated at over 0.4 without a corresponding significant increase in carbon monoxide or CO make.

- A valid trigger is defined as any data where the theoretical Graham's ratio is calculated at over 0.4 with a corresponding significant increase in raw carbon monoxide or CO make associated with the data. By definition any Graham's ratios over 0.4 which are not valid triggers are considered invalid triggers.

Filtering of minimum oxygen deficiencies

After processing, each set of data was subject to filtering of the measurements based on the corresponding minimum oxygen deficiency being tested. The following information was obtained by comparing filtered data, initial data and reported data from the monitoring system.

- Overall data retention
- Retention of normal data
- Investigate data removed
- Invalid data eliminated
- Valid data eliminated

These values were recorded for each processed dataset and compiled to produce average results for locations of similar type and analytical technique.

RESULTS AND DISCUSSION

Tube bundle data for a three month period at numerous underground locations was processed. The locations investigated were longwall tailgates, goaf seals, main roads and return roads. Measured values were used for the initial gas for some locations. Real time monitoring data for one week was processed from three locations including one longwall tailgate and two main gate locations. All locations were interpreted for valid triggers by identifying any increase in raw carbon monoxide value or carbon monoxide make corresponding with Graham's ratios over 0.4.

Tube bundle: Longwall Tailgate return

The data reported in Table 2 shows that an oxygen deficiency filter of 0.05% or 0.1% retained more data and potential valid triggers than the gas monitoring system reported. The reported gas monitoring data removed 100% of the invalid triggers, however almost 75% of overall data was filtered as well. An oxygen deficiency filters of less than 0.3% and higher than 0.05% appears to be optimal for these locations. A minimal oxygen deficiency of 0.3% was proven to be too high for these locations as the majority of the data was removed, similar to the data reported by gas monitoring software.

Table 2 Longwall Tailgate Return - theoretical initial air

Filter	Average Retention of normal data (%)	Average investigate data removed (%)	Average Invalid triggers removed (%)	Valid triggers removed (%)	Total data sets
Gas monitoring system reported	25.8	82.1	100.0	100	2.0
minimum 0.05%	93.6	35.0	95.2	0	2.0
minimum 0.1%	66.3	58.9	96.8	20	2.0
minimum 0.3%	27.7	100.0	100.0	100	2.0
total valid triggers				5	

Table 3: Longwall Tailgate Return - measured initial air

Filter	Average Retention of normal data (%)	Average investigate data removed (%)	Average Invalid triggers removed	Valid triggers removed (%)	Total data sets
Gas monitoring system reported	25.8	87.5	100.0	50.0	2.0
minimum 0.05%	96.4	38.1	98.7	0.0	2.0
minimum 0.1%	49.3	82.8	100.0	100.0	2.0
minimum 0.3%	20.6	100.0	100.0	100.0	2.0
total valid triggers				2	

Tube bundle: Main road and seals

Testing of tube bundle gas monitoring results from both the mains and seals reflected a similar outcome to the longwall tailgate results with a minimum oxygen deficiency of 0.05% appearing to be optimal value for retention of data and elimination of invalid triggers. Application of 0.1% and 0.3% resulted in an unacceptable data loss of valid triggers and overall data. Using a measured initial air value decreased the rate of valid and invalid data.

Real Time: Longwall return and Mains

Similarly to the tube bundle data, 0.05% and 0.1% minimum oxygen deficiency outperformed the measured reported data in terms of data retention (Real Time: Longwall return and mains Table 4). In contrast the minimum oxygen deficiency of 0.05% was not high enough to filter out enough of the invalid readings for practical application. Due to the frequency of real time measurements taken, this would not be sufficient to prevent an excessive number of false alarms. An oxygen deficiency of 0.1% was able to remove all of the invalid triggers while retaining all of the valid triggers and 76.7% of the overall data. It is recommended that an oxygen deficiency filter greater than of 0.05% should be used for real time systems.

Table 4: Real time - longwall return and mains

Filter	Average Retention of normal data (%)	Average investigate data removed (%)	Average Invalid triggers removed (%)	Valid triggers removed (%)	Total data sets
Gas monitoring system reported	64.9	65.1	100.0	75.0	3.0
minimum 0.05%	99.7	21.4	56.7	0.0	3.0
minimum 0.1%	76.7	36.9	100.0	0.0	3.0
minimum 0.3%	50.3	75.0	50.0	66.0	3.0
total valid triggers				12.0	

Real time data generated excessive investigate triggers compared to tube bundle results making the technique less suitable for effective trending.

CONCLUSION AND RECOMMENDATION

- Tube bundle data is more effective for trending Graham's ratio than real time.

- A minimal overall oxygen deficiency of less than 0.3% will improve data retention and still have effective removal of invalid triggers for tube bundle calculated Graham's ratio trends compared to the current process of filtering.
- An optimal minimal overall oxygen deficiency for real time calculated Graham's ratio lies between 0.1% and 0.3%. Further investigation to determine optimal value is recommended.
- A minimal oxygen deficiency of 0.3% leads to an indiscriminate loss of potentially valid data for atmospheres close to air, without a decrease in false alarms in atmospheres with low oxygen deficiency.
- Implementation of these optimal tested values should be considered for trial and further review.
- Further testing and investigation should be done to determine an optimal theoretical oxygen deficiency filter.

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