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

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#### **Gas Data**

- The average control room receives over 50 000 gas results each day.
- The majority of these are from real time monitoring.
- Nearly 1000 measurements made by the tube bundle.
- Variable numbers of bag samples collected for GC analysis





#### **Real Time**

- Ideal for telling us what is happening now, they offer real time warning.
- Sensors are exposed to the harsh underground environment, not ideal for analytical measurements.
- Detect step changes, such as the onset of a fire, products from an explosion, a sudden increase of seam gas in the general body or reduction in oxygen.



#### **Real Time**

- Limited measuring ranges: carbon monoxide often only up to 50ppm, methane to 5% and carbon dioxide to several percent.
- 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.
- Issues with cross sensitivities.





- 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.



- The ability to measure CO down to 1ppm, long term stability and frequent automated sampling ,makes this technique best for long term trending of carbon monoxide, or carbon monoxide make, to identify a spontaneous combustion event.
- Most systems only capable of measuring carbon monoxide to only 1000ppm.



 This technique is the best for monitoring explosibility during a routine sealing operation so long as a fire or heating doesn't exist.





- 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.
- Each point may only be sampled once every thirty to sixty minutes.
- Not suitable for the instantaneous detection of an incident such as a fire.





 Measurement of oxygen using paramagnetic analysers is flow rate dependent so flows from all tubes must be balanced.



 Two locations with the same oxygen concentration could read differently because more resistance in one of the tubes results in a slower flow and subsequently a lower reading than a location with the same concentration but flowing through the instrument at a faster rate.



 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.





- GC is not going to be suitable for detection of a belt fire because of the time delay
- Delay is acceptable for evidence and trending of spontaneous combustion indicators.





The GC is not the best technique for low concentrations of carbon monoxide, therefore this technique is not the preferred method for determination of carbon monoxide makes.
So long as calibration gases available no maximum to what can be measured.



 During a significant spontaneous combustion event, fire or following an explosion, it is the only technique that will allow an accurate determination of the explosibility of the underground environment because it measures the hydrogen and high carbon monoxide concentrations.





#### Real Time vs Tube Bundle Oxygen





#### **Real Time vs Tube Bundle CO**





#### Tube Bundle vs GC Oxygen





#### **Tube Bundle vs GC CO**



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#### **Tube Bundle vs GC CO<sub>2</sub>**





#### **Tube Bundle vs GC Methane**



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 Several of the ratios commonly calculated from results generated from all three techniques used to determine the status of any spontaneous combustion activity require determining the oxygen deficiency.



 Oxygen deficiency is the amount of oxygen consumed/removed and is often determined using the following equation:

Oxygen deficiency =  $0.265 \times N_2 - O_2$ 



- This equation is based on the assumption that nitrogen is inert and won't be consumed or created.
- If the initial gas entering the area had the 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.



 The use of the fresh air nitrogen concentration of 79.02% includes argon and is only valid for techniques unable to differentiate the two gases.

 Eliminates most problems associated with dilution because the measured nitrogen has also been diluted.



# • Effective 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.



Measured Oxygen %	Measured Nitrogen (including Argon) %	Calculated Initial Oxygen (0.265xN <sub>2</sub> ) %	Calculated Oxygen Deficiency (0.265xN <sub>2</sub> - O <sub>2</sub> ) %	Calculated Oxygen Deficiency (20.95- O <sub>2</sub> ) %
2.3	81.8	21.68	19.38	18.65
9.2	80.4	21.31	12.1	11.75
15.7	83.1	22.02	6.32	5.25
8.1	89.1	23.61	15.51	12.85



#### **Grahams Ratio**





 GC is the only method of analysis that actually measures the nitrogen, giving added confidence in ratio calculations.

 Because the fresh air ratio without including argon with the nitrogen, is 20.95% oxygen to 78.1% nitrogen (20.95/78.1=0.268).

• Oxygen deficiency =  $0.268 \times N_2 - O_2$ 



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



#### **Calculated Initial Oxygen**



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#### **Graham's Ratio**





 Ratios including Graham's Ratio, that incorporate oxygen deficiency can be unreliable for samples where oxygen deficiencies are less than 0.3%.



#### **Real Time vs Tube Bundle O<sub>2</sub> Deficiency**



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#### Graham's Ratio Tube vs Real Time





#### Fresh Air as Measured by Tube Bundle





 Oxygen deficiency is not just a reduction in oxygen concentration caused by dilution with seam gases but the "consumption" of oxygen.



 The ratios using this parameter are determining "how much" products of combustion are being produced for how much oxygen is being used.



 As coal gets hotter, the efficiency of the reaction increases with more products produced for less oxygen consumed.



#### Graham's Ratio Calculations

Introduced Methane	Initial Oxygen Concentration	Oxygen Measured	Carbon Monoxide	Graham's Ratio
	(%)	in Sample	Measured in	100xCO/
		(%)	Sample (%)	(20.95-O <sub>2</sub>
				Measured)
	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



#### Graham's Ratio Calculations

Introduced Methane (%)	Measured Nitrogen Concentration (%)	Oxygen Measured in Sample (%)	Carbon Monoxide Measured in Sample (%)	Graham's Ratio Using Equation*
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

\*GR =  $\frac{100x(COf-(N2f/N2i)xCOi)}{((N2f/N2i)xO2i - O2f)}$  where i is initial and f is final



#### **Measurement Errors**

 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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Customer Simtars Wacol 15593 Cylinder # 456985 Tony Kelly Cylinder size G 6.6m<sup>3</sup> at 15°C & 101.3kPa

**Reference Material Report** 

Component	Result	Method
Helium	114±4ppm	7-4
Ethylene	114±3ppm	5-1
Ethane	120±3ppm	5-1
Hydrogen	204±8ppm	7-4
Carbon Monoxide	189±5ppm	5-1
Carbon Dioxide	0.98±0.02%	5-1
Methane	0.94±0.02%	5-1
Oxygen	19.6±0.5%	8
Nitrogen	Balance	

Expanded uncertainty stated is calculated using a coverage factor of 2, providing a level of confidence of approximately 95%

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Air Liquide Australia Limited 40 Bunnet Street, North Sunshine, Victoria 3020 Phone (03) 9290 1155, Fax (03) 9290 1173 U0015



Measured Oxygen (%)	Measured Nitrogen (%)	Excess Nitrogen $N_2$ - ( $O_2$ x3.728) (%)
20.98	78.02	-0.19
20.84	77.56	-0.12
20.91	77.80	-0.14
20.99	78.02	-0.23



Measured	Measured	Excess	Oxygen
Oxygen	Nitrogen	Nitrogen	Required
(%)	(%)	$N_2$ - ( $O_2$ x3.728)	For Positive
		(%)	Nitrogen
			Excess
			(%)
20.98	78.02	-0.19	20.92
20.84	77.56	-0.12	20.80
20.91	77.80	-0.14	20.87
20.99	78.02	-0.23	20.92



Measured	Measured	Excess	Nitrogen
Oxygen	Nitrogen	Nitrogen	Required
(%)	(%)	$N_2$ - ( $O_2$ x3.728)	For Positive
		(%)	Nitrogen
			Excess
			(%)
20.98	78.02	-0.19	78.21
20.84	77.56	-0.12	77.68
20.91	77.80	-0.14	77.94
20.99	78.02	-0.23	78.25





Measured Oxygen (%)	Measured Nitrogen (%)	Excess Nitrogen N <sub>2</sub> - (O <sub>2</sub> x3.728) (%)	Oxygen Required for Positive Nitrogen Excess	Nitrogen Required for Positive Nitrogen Excess
20.98	78.02	-0.19	20.94	78.10
20.84	77.56	-0.12	20.82	77.62
20.91	77.80	-0.14	20.89	77.88
20.99	78.02	-0.23	20.95	78.10







#### Airfree

• Airfree calculations are effective for removing the influence dilution with air has on the sample.



#### Airfree

 Calculations from samples consisting of mostly air must be used with caution as any errors in measurement of remaining gases are magnified.



#### Airfree

 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.



#### **Determination of Explosibility**

 Due to the percentage concentrations of carbon monoxide and hydrogen that can be produced during a significant spontaneous combustion incident or fire, any assessment of explosibility must be done using GC results.



#### Explosibility



Gas Mix; 1.26%H2, 10.45%O2, 78.85%N2, 3.93%CH4, 1.82%CO, 3.66%CO2, 130ppmC2H4, 179ppmC2H6



#### Explosibility



## Gas Mix; 2.90%H2, 7.51%O2, 78.45%N2, 1.38%CH4, 2.02%CO, 6.67%CO2, 480ppmC2H4, 1082ppmC2H6





## Gas Mix; 6.48%H2, 6.48%O2, 73.17%N2, 1.99%CH4, 2.33%CO, 15.07%CO2, 1152ppmC2H4, 774ppmC2H6



 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 operating them and using the generated results for interpretation.



 There are always errors and uncertainties associated with gas measurements.



 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.

