How Well Can We Cope With Gas Analysis During a Mine Fire?

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Abstract

Assessment of the underground atmosphere during a mine fire or spontaneous combustion event is best done using results generated by gas chromatography. Much effort has gone into establishing gas chromatograph systems to detect the onset of any such event. Most of the samples analysed return results within normal parameters, so operators are rarely exposed to the analysis of mine fire type samples.

Gas chromatographs were initially introduced at mine sites to provide analytical support during a mine emergency, but advances in the technique have provided indicators for the early detection of spontaneous combustion. Does this mean that we have moved away from the initial intent of having gas chromatographs onsite?

This paper examines the results and makes recommendations from proficiency testing designed and conducted to assess the capability of mines to analyse samples likely to be generated in the event of a mine fire or serious spontaneous combustion event.

Introduction

It has been over twenty years since a "further recommendation" by the Warden's Inquiry into the 1986 Moura No. 4 Mine Disaster called for mines rescue stations in Queensland to be equipped with a gas chromatograph (GC). This followed problems during mine emergencies with the operation of supposedly portable units that were brought to site and the delays in receiving results for samples transported to established analytical laboratories.

History shows us that the Warden's recommendation was not implemented exactly as intended, but that perhaps a more effective approach was adopted where GCs were installed at each underground mine rather than at rescue stations. It was possible to go further than the Warden intended due to the incorporation of communication capabilities on board the GC for the first time. This allowed Simtars' experienced gas chemists to oversee GC operation remotely and thereby reduced the expertise required of mine site personnel and enabled the ongoing trouble free operation of this complex analytical equipment on site.

When first installed in the late eighties, analysis time for one sample could be between twenty and thirty minutes. This did not lend itself to the analysis of large numbers of samples. Furthermore, the sensitivity of these earlier instruments was not necessarily good enough to detect the early onset of spontaneous combustion. The GCs were there with the primary purpose of being used in a mine emergency.

With improvements in technology and the development of micro GCs, analysis time has dropped to several minutes and detection limits have improved greatly. This has resulted in mines using GC analysis to conduct routine assessments of the underground environment. As such the role of the GC has shifted from gas analysis during emergencies to everyday assessment of the underground environment.

Mines don't rely solely on GC analysis but use a combination of real time sensors, tube bundle analysers and GC analysis. This provides a comprehensive assessment of the state of the underground atmosphere. Each technique has its own limitations but these are admirably compensated for by the strengths of the others to identify immediate and developing situations.

GC analysis is the only technique available on a mine site which provides complete analysis of gas composition by accurately quantifying all components of a gas mixture. GC has the capability to analyse the full analytical range (0-100%) of each component, and does not suffer problems of cross sensitivity as each analyte is separated as part of the analysis. A typical analysis includes helium, hydrogen, oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, ethylene and ethane.

During a mine fire or advanced spontaneous combustion event it is not uncommon for percent levels of hydrogen and carbon monoxide, several thousand parts per million of ethane and several hundred parts per million of ethylene to be produced. These gases significantly influence the explosibility of the gas mixture which can no longer be assessed on methane concentration alone. Levels of this magnitude exist only during a fire or spontaneous combustion event, and as such the majority of mine workers will have no experience in analysing or interpreting these kinds of samples. Inaccurate assessment of a mines' atmosphere during a spontaneous combustion event has resulted in the deaths of mine workers in the past.

Hydrogen, nitrogen, ethylene and ethane are unable to be detected by any commonly available and reliable technique other than GC. Most mine site carbon monoxide analysers are also limited to a maximum of 1000 ppm, leaving GC as the only technique capable of quantifying carbon monoxide above this level. For these reasons, to accurately assess the explosibility of a mine atmosphere during a fire or spontaneous combustion event a GC must be utilised. Furthermore, accurate quantitation of nitrogen is necessary for the assessment of the state of fire or heating using gas ratios such as Graham's, Young's. and the Jones-Trickett's ratio. This can only be achieved using a GC.

Figure 1 shows a Coward triangle of actual mine fire data as it would be measured using a tube bundle system. The tube bundle system will report this sample to contain 7.51% oxygen, 1.38% methane, 1000 ppm carbon monoxide, 6.67% carbon dioxide and 84.35% nitrogen (not measured but calculated by difference). The Coward triangle suggests this sample is not explosive, as indicated by the cross in the non-combustible section of the triangle.

Figure 1 – Coward triangle for fire gas analysed by tube bundle system.

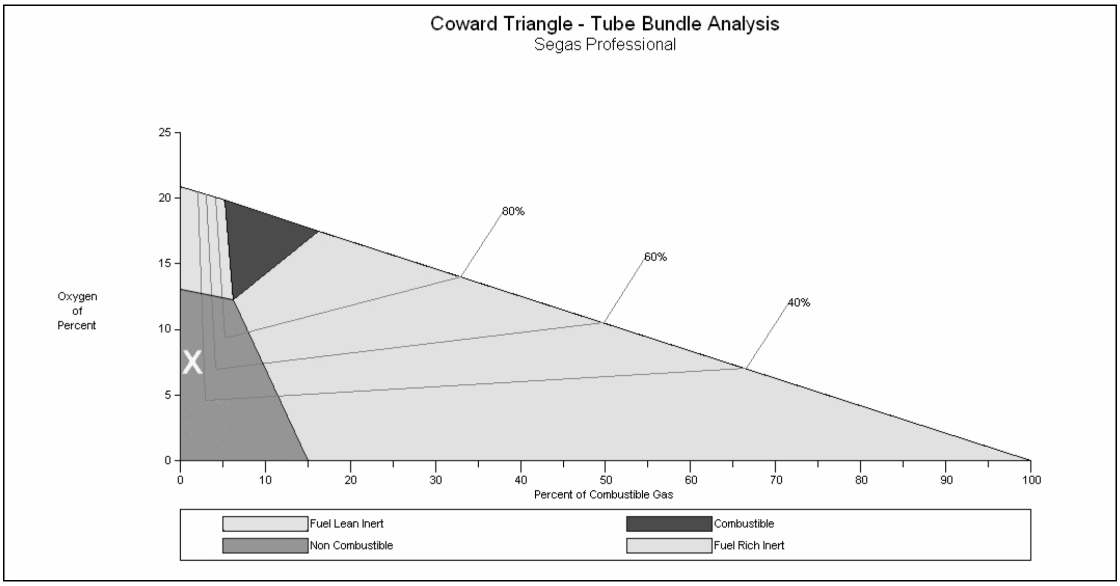
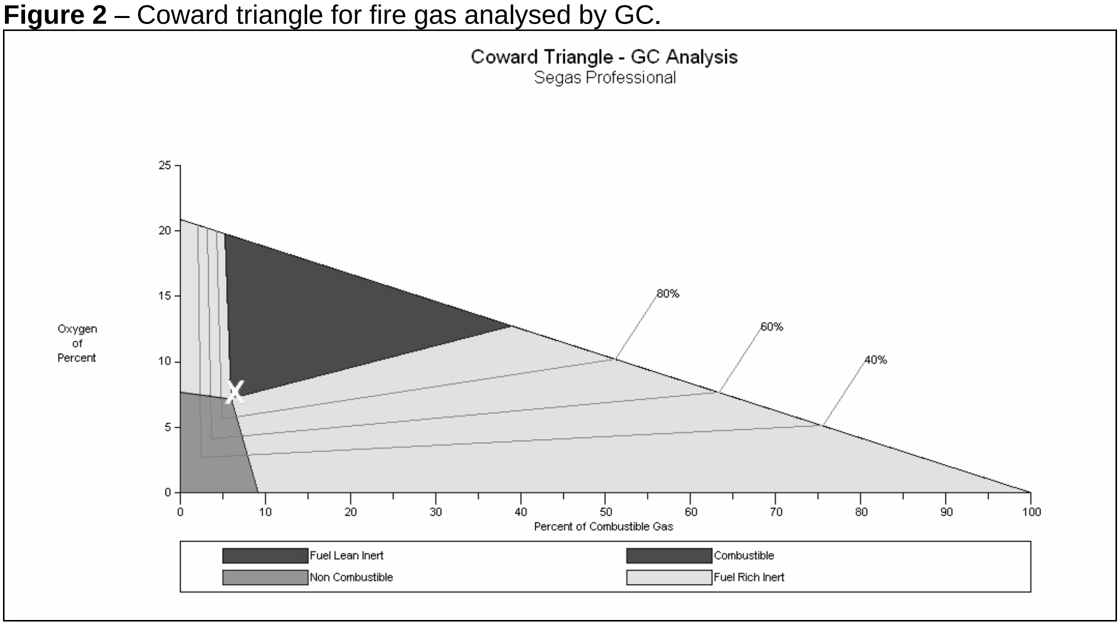


Figure 2 shows a Coward triangle of the very same sample but this time it has been analysed on a GC. The GC assessed this sample to contain 2.9% hydrogen, 7.51% oxygen, 78.45% nitrogen (measured this time not calculated by difference), 1.38% methane, 2.02% carbon monoxide, 6.67% carbon dioxide, 480 ppm ethylene, 1082 ppm ethane and 0.91% argon. This time the Coward triangle paints an entirely different picture. It shows that the same sample the tube bundle analysis said was safe is, in fact, explosive as indicated by the cross in the combustible section of the triangle. The size of the explosive zone of the Coward triangle is significantly larger than that from the tube data due to the influence of the gases unaccounted for by the tube bundle system.

Figure 2 – Coward triangle for fire gas analysed by GC.



This example clearly demonstrates the importance of analysing fire gas samples using a GC, as the tube bundle system provides a completely different and in this case inaccurate assessment of the explosibility of the mine atmosphere. An oversight like this during an actual fire scenario could cost lives.

Testing Program

Following concerns raised within the coal mining industry with respect to the ability of mines to analyse samples during mine emergencies, Simtars set about establishing what capability they had. Simtars developed a testing program for users of its GC based Computer Assisted Mine Gas Analysis System (Camgas). All Camgas GCs have a preconfigured and calibrated mine fire method tested by Simtars on a regular basis. It has also been Simtars' recommendation that Camgas sites acquire their own calibration gas for this method containing 3% hydrogen, 3% carbon monoxide and 12% carbon dioxide in a balance of nitrogen. Simtars has made a cylinder of this mixture available at the Dysart mines rescue station as an emergency backup, however having a cylinder immediately available on site is a much better option. The other gases likely to be present are adequately covered by the regular span gases used.

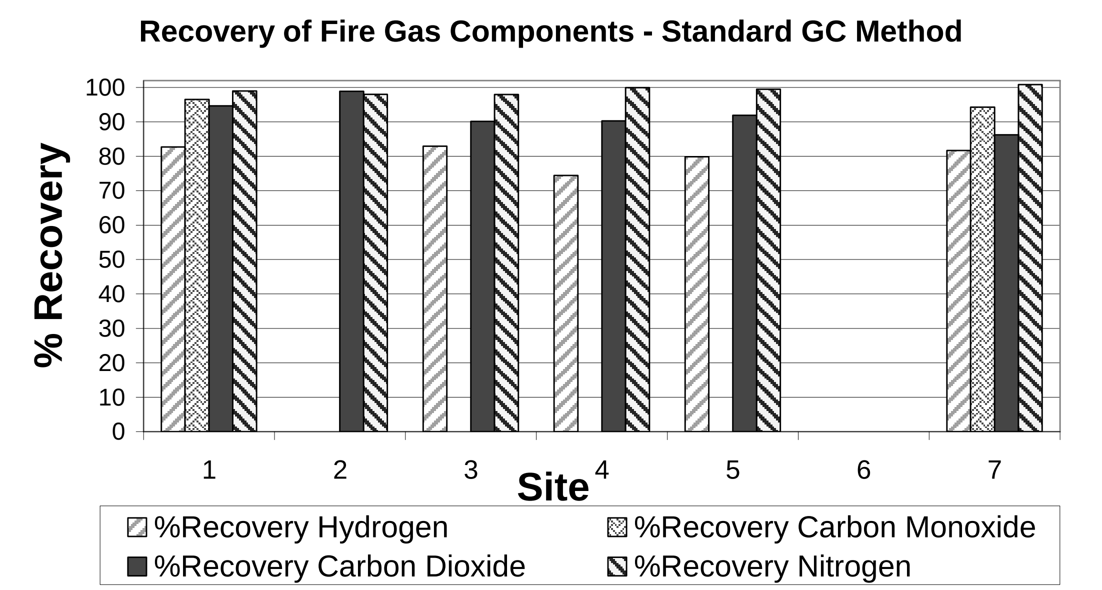
Camgas equipped sites were requested to analyse a sample on both their standard GC method and their mine fire method. For safety reasons the sites were advised that the sample contained very high concentrations of carbon monoxide, but only Simtars knew the true concentration of each of the components. The test gas was a mixture containing 2.93% hydrogen, 3.54% carbon monoxide, and 11.9% carbon dioxide in a balance of nitrogen. Sites were requested to report their results and complete a short questionnaire on any problems or difficulties they had in completing the analysis. Sites with their own mine fire span were requested to calibrate the method fully prior to use. Sites without access to a fire span were requested to calibrate with the gases they had available, and run the sample without calibrating the fire span points, under Simtars supervision. This is the situation these sites would find themselves in during an actual emergency until the Simtars cylinder arrived on site, but with remote, expert support provided by Simtars which is always available around the clock.

Results

Table 1 – Site Results

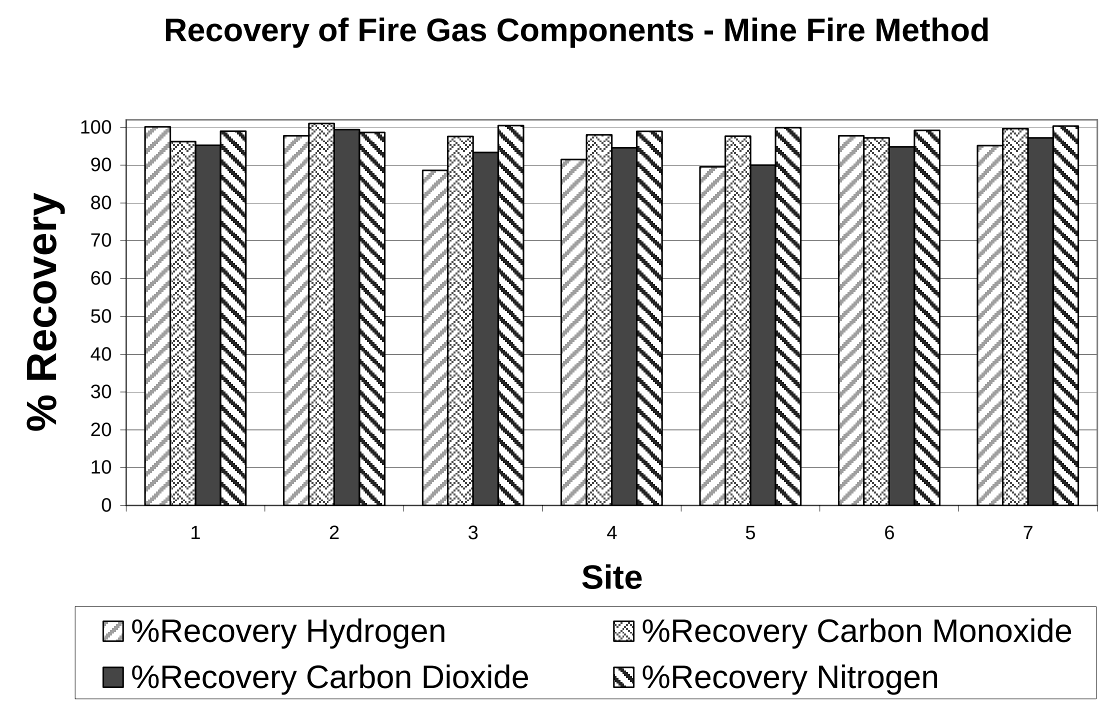
		Hydrogen (%v/v)	Carbon Monoxide (%v/v)	Carbon Dioxide (%v/v)	Nitrogen (%v/v)	Calculated LEL (%)	Calculated UEL (%)
Certified Values		2.93	3.54	11.90	81.63	6.37	74.56
	Method						
Site 1	Standard	2.42	3.42	11.26	80.79	6.64	74.52
	Fire	2.93	3.41	11.34	80.84	6.30	74.56
Site 2	Standard	Saturated	Saturated	11.77	79.98	-	-
	Fire	2.87	3.58	11.83	80.52	6.43	74.55
Site 3	Standard	2.43	Saturated	10.72	79.93	-	-
	Fire	2.60	3.46	11.11	82.07	6.54	74.54
Site 4	Standard	2.18	Saturated	10.74	81.59	-	-
	Fire	2.68	3.47	11.26	80.77	6.49	74.54
Site 5	Standard	2.34	Saturated	10.94	81.20	-	-
	Fire	2.62	3.46	10.72	81.58	6.52	74.54
Site 6	Standard	Not Reported					
	Fire	2.86	3.44	11.29	80.99	6.36	74.56
Site 7	Standard	2.39	3.34	10.26	82.32	6.73	74.52
	Fire	2.79	3.53	11.57	81.90	6.45	74.55

Graph 1

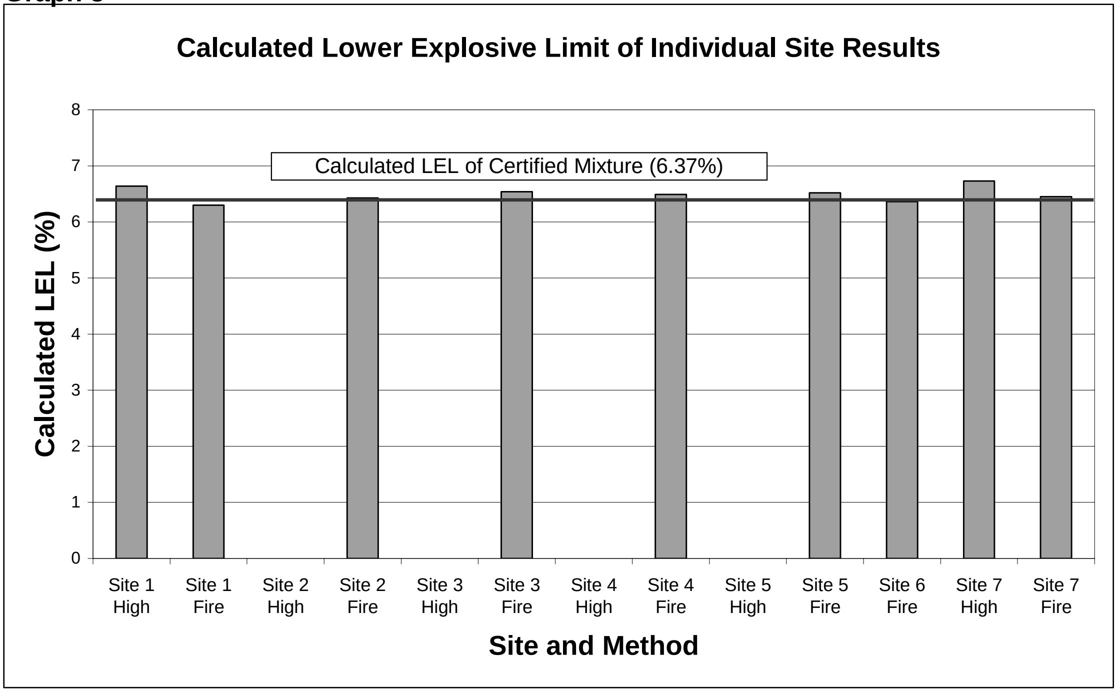


Missing results indicate instances where the detector reached maximum range for the method settings, and was unable to analyse the component on the standard method, except for site 6 that only ran the sample using the mine fire method.

Graph 2



Graph 3



Graph 4

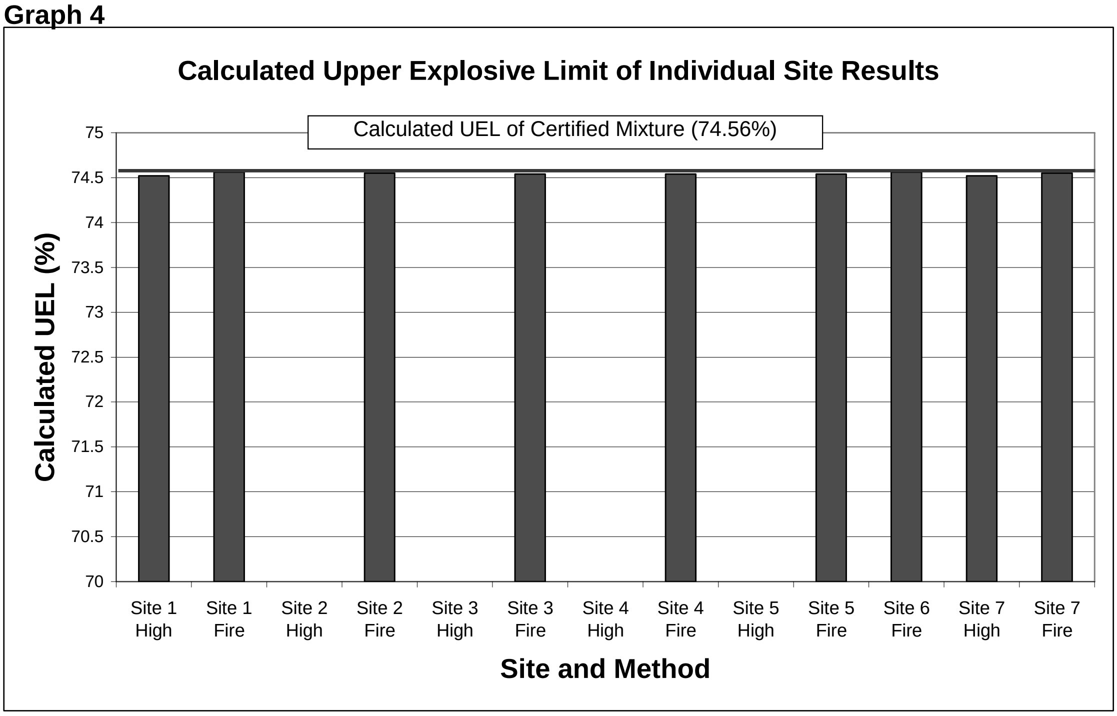
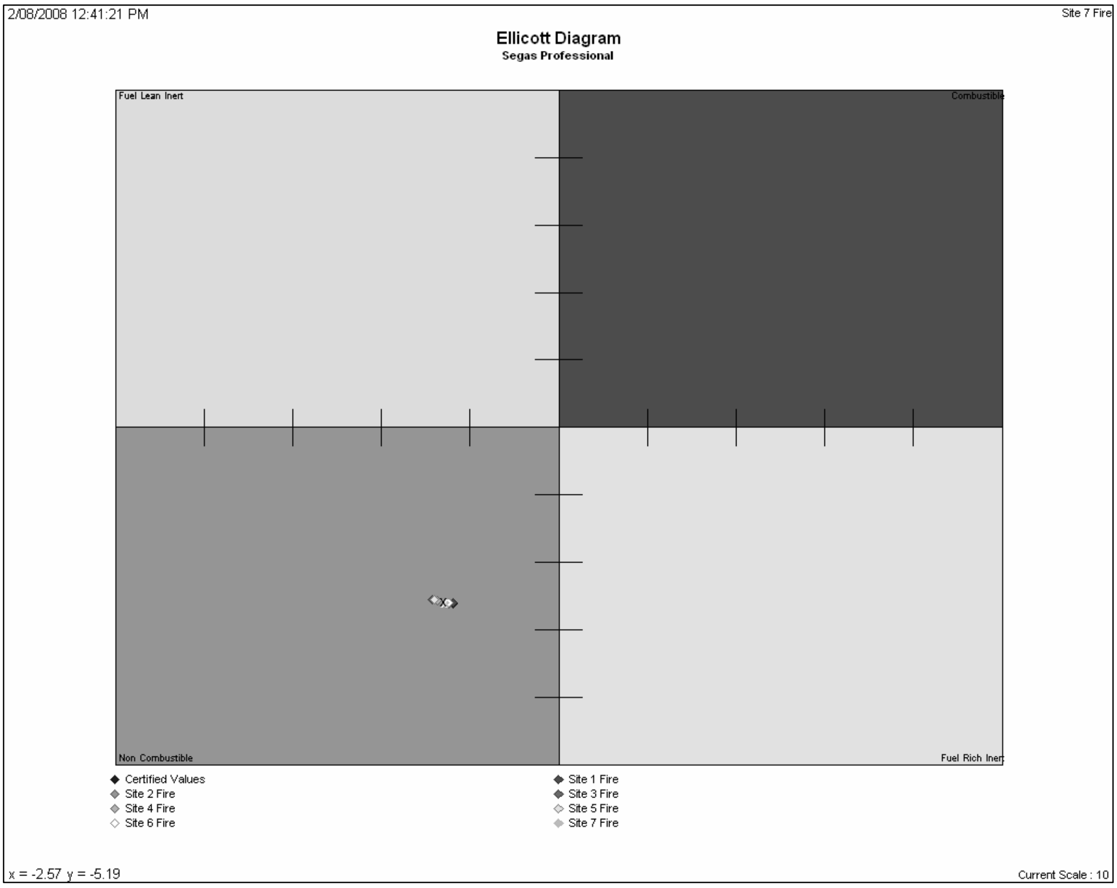


Figure 3 – Ellicott diagram for mine fire method results



Discussion

Camgas utilises Agilent micro GCs of the Quad and 3000 series. The quad series instruments (1997-2004) utilise a detector in which the attenuation is set within the method at one of three ranges, high, medium or low. This means components may saturate on the medium or high sensitivity if they exceed the maximum concentration for the detector setting, and require re-analysis on a method using a lower detector sensitivity. The mine fire method is configured using detector settings which will enable analysis of the full anticipated range, whilst the standard GC method is configured for maximum sensitivity of components under normal circumstances. The 3000 series instruments (2004-present) have alleviated this issue with a new detector with a wide dynamic range.

As expected most of the sites using Quad series GCs experienced problems with saturating the detector when using the standard method. As such they were unable to quantitate all of the components in the sample sent when using these methods. Use of the mine fire method eliminated this problem. This issue aside, Table 1 and Graphs 1 and 2 clearly show that the accuracy in determining the composition of a sample with percentage levels of hydrogen and carbon monoxide is significantly improved by using the mine fire method. This improvement was seen regardless of whether or not the method was calibrated using a mine fire span. Only sites 4, 6 and 7 made use of a mine fire span. The remaining four sites relied on standard span gases with a previously calibrated mine fire span point.

The significance of the accuracy of the results generated using the mine fire method can be seen in Graphs 3 and 4 and Figure 3. Graphs 3 and 4 show the lower explosive limit (LEL) and the upper explosive limit (UEL) respectively, as calculated from the results generated and compared to the true values for the samples analysed. All sites returned results close to the true values. Using the results from any of the sites would return calculated explosive limits suitable for assessment of the explosibility of the underground environment. The determination of these limits is dependent on the ratio of the flammable gases. Correct values could be calculated from results that were analysed incorrectly so long as the ratio of flammable gases remained the same. This situation could occur if the operator introduced air into the sample through poor sample introduction technique or if there was a leak in the introduction system to the GC.

Figure 3 goes further and shows where all of the samples analysed lie on an Ellicott diagram, including the true position of the test mix used. All points are in close proximity and within the same region of the Ellicott diagram. This is a better reflection of the correct assessment of the explosibility as it requires the measured concentrations to be correct to be positioned correctly on the diagram, and not just the ratio. The positioning of the points on the Ellicott diagram show that the results generated using the mine fire method on Camgas systems are suitable for assessment of the explosibility of the underground environment.

The sites that did not calibrate the mine fire method with a mine fire span on the day of analysis relied on a previous calibration. While all returned totally acceptable results, this success is based on the instrument response remaining relatively unchanged between the calibration of this point and the running of any samples. This can never be guaranteed and is why this approach should only be adopted under the supervision of Simtars gas chemists. It is preferential for all sites to have immediate access to mine fire spans for calibration.

Conclusions

The mine sites that participated in this testing program clearly demonstrated the ability to analyse samples containing percent levels of carbon monoxide and hydrogen to enable an accurate assessment of the flammability of the atmosphere typical in mine fires or advanced spontaneous combustion events.

The use of a dedicated method for the analysis of samples from a mine fire improves the accuracy of the analysis.

Using a span gas to calibrate the instrument response to the high levels of hydrogen and carbon monoxide at the time of analysis can improve accuracy and give greater confidence in the results.

References

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