Fast On-Site Mine Safety Analysis using a Micro Gas Chromatograph

Numerous mine disasters with loss of many lives continue to occur today. This fact dramatically emphasises the importance of fast and accurate determination of the mine atmosphere, to provide early warning of hazards in day-to-day mine operations. Accurate determination is also important for ensuring safety after an accident has happened. This article describes a method for fast on-site analysis of mine gases in less than 100 seconds using a micro gas chromatograph equipped with four independent column channels.

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We all can recall the news bulletins reporting a mine accident and, in some cases, the many lives that are lost. Globally, mining disasters continue to occur almost every week from explosion, fire, flood or collapse [1]. Therefore, an early warning system for fast analysis of the mine atmosphere is extremely important for day-to-day mining activities. Moreover, a complete overview of the gases in the mine, after an accident, is essential to determine if the mine is safe for a rescue team to enter.

First, it is necessary to check for explosive gases in a mine environment. During the formation of coal beds some gases, mainly methane and some ethane and hydrogen, are trapped in the coal. When these coal beds are then mined the gases are released, which can pose a danger as methane and other mine gases, when mixed with oxygen from the air, are highly explosive. To prevent explosion hazards, it is necessary to monitor flammable gases such as methane, hydrogen, and the C2 hydrocarbons. A second reason for mine gas analysis is to ensure the absence of carbon monoxide and the right oxygen and carbon dioxide levels in the mine atmosphere, which is critical for the safety of mine workers and rescue teams. Third, analysing the gases in a mine can predict spontaneous combustion or detect the early stages of a fire. Spontaneous combustion could occur when internal heat, produced by chemical reactions in the coal, is generated faster than it can be lost to the surrounding environment – which can be monitored by measuring specific gases in the mine. Hydrogen and ethylene are formed when temperatures rise above 100°C, and the presence of low concentrations of these gases gives an indication of fire or elevated temperatures. Detecting possible hazards early increases the chance of successfully dealing with the problem. The Safety in Mines Testing and Research Station (SIMTARS), based in Queensland, Australia, has been providing and supporting gas monitoring systems based on gas chromatographs to the mining industry for over 20 years. Further, SIMTARS offers services, support, and training to mining companies to reduce the risks of mine explosions and help them after a mine disaster. This article describes the methodology and equipment used to provide a complete, fast, and on-site analysis of the gases collected from an underground mine.
Experimental setup and conditions

The analysis described below uses a 490 Micro GC (Agilent Technologies, Inc.), which consists of a quad cabinet and is equipped with four independent column channels. Each column channel is a complete, minimised gas chromatography (GC) with electronic carrier gas control, micro-machined injectors, narrow-bore analytical columns, and micro-thermal conductivity detector (µTCD).

The first channel installed is equipped with a 10 meter CP-Molsieve 5Å column, running on argon as carrier gas, for the analysis of helium, hydrogen, oxygen, and nitrogen. Channels 2 and 3 are identical and, like the first channel, are equipped with a 10 meter CP-Molsieve 5Å column. However, these channels have the optional backflush functionality and run on helium carrier gas, for the analysis of methane and carbon monoxide. Ethane and ethylene are analysed on a fourth channel using a 10 meter PorapLOT U column. For full details of the analytical conditions for all channels, see the methodology application note, available online [2].

ECD Chromatography Data Software (Agilent Technologies, Inc.) is used for data acquisition, and EZGas Professional software (SIMTARS), specifically written for the mining industry, is used for calibration and result generating. The analysis results are exported to Segas Professional (SIMTARS) for additional combustibility calculations, combustion ratio and trend analysis.

Fast mine safety analysis in less than 100 seconds

The first column channel, equipped with a CP-Molsieve 5Å column, is used to analyse permanent gases, including helium, hydrogen, oxygen and nitrogen. Figure 1 shows a chromatogram where the compounds of interest are well separated. The molecular sieve channel runs on argon as the carrier gas, which enables the determination of low concentrations of helium and hydrogen. When argon is used as a carrier gas compared to helium, all other compounds will have an increased detection limit by approximately a factor of 10. However, oxygen and nitrogen are present at percentage levels in the mine atmosphere, which allows the use of argon carrier gas for detection of these gases.

Concentration results for hydrogen, oxygen, and nitrogen are used for combustibility calculations. Helium, naturally available in the atmosphere at low ppm concentrations, is analysed on this channel as well. On a molecular sieve column, helium and hydrogen elute close together. Analysis of helium prevents it from being incorrectly reported as hydrogen, which can result in the erroneous conclusion that spontaneous combustion is occurring. Helium may also be used as a tracer gas to determine gas movements in the underground mine. Channel two also includes a 10 meter Molsieve 5Å; this time with helium as the carrier gas. This channel is used for the analysis of methane and carbon monoxide. Figure 2 shows a chromatogram for two different samples, one containing a medium level for carbon monoxide (~200 ppm) and the other with a very low level of carbon monoxide. In this chromatogram, excellent separation and analysis of methane and carbon monoxide is obtained in less than 100 seconds.

The typical limit of detection for the µTCD is 1 ppm for early eluting components on a Wall Coated Open Tubular (WCOT) column and 10 ppm on Porous Layer Open Tubular (PLOT) and micro-packed column types. The CP-Molsieve 5Å column is a PLOT-type column, however when it comes to carbon monoxide at low levels, the exact concentration is of less importance than the trend. Even a slight increasing trend of the chromatogram’s baseline at the carbon monoxide retention time is monitored for early indications of spontaneous combustion in the mine. This Molsieve 5Å channel is equipped with backflush functionality to ensure moisture, carbon dioxide, and the C2 hydrocarbons are backflushed to vent, to maintain the separation efficiency of the molecular sieve column. Moisture and carbon dioxide tend to adsorb quickly to the Molsieve 5Å stationary phase changing its chromatographic properties. This could result, over time, in retention shifts and loss of separation. For SIMTARS, the analysis of methane for explosion risk reasons and carbon monoxide for combustion identification are of high importance, especially when the Micro GC is taken into the field after a mine disaster. Therefore, this column channel is duplicated to the third position of the instrument to allow optimised operation for the analysis of each, and to have a backup column available at all times. When one column is reconditioned, the other column can still be used for analysis.

The fourth channel, equipped with a 10 meter PorapLOT U column and helium as the carrier gas, is used to analyse carbon dioxide, ethane, and ethylene. Figure 3 shows an example for baseline separation of these three components. The right carbon dioxide level is of importance for the safety of the mine workers and rescue personnel. Moreover, the results for carbon dioxide and ethane are also used in the combustibility calculations by SIMTARS. As mentioned above, ethylene and hydrogen are formed when coal temperatures rise above 100°C and are therefore used as an early warning for spontaneous combustion or a fire.

Excellent repeatability for quantity and retention time

Repeatability, reported as relative standard deviation, shows excellent results for both concentration and retention time. For full details, see the methodology application note, available online [2]. Typical values, based on quantity, are determined around 0.05% RSD for components that are present in the sample at percentage levels and between 0.1 to 0.6% for ppm level components. Retention time repeatability, for all components of interest, is calculated at 0.01% or lower.

Conclusion

The 490 Micro GC is a powerful tool for accurate mine safety analysis, and it provides a complete, fast and on-site analysis of the mine gases collected from underground. Moreover, the system detects compounds that are not covered by the mine’s continuous monitoring system. Using an analysis system that determines mine environment samples in less than 100 seconds resulting in multiple results per hour for accurate trend analysis allows better informed decision making for the prevention of mine disasters. In addition, such analysis provides rapid and reliable results to determine, after a mine disaster, the status of the underground environment before deciding to send in a rescue team.

References
