EMERGING TECHNOLOGY IN GAS MONITORING EQUIPMENT By Mr Colin Hester B.App Science - Supervising Chemist and Mr Stewart Bell B.App Science, C.I.C., M.A.I.O.H. - Manager Occupational Hygiene, Environment & Chemistry Centre SIMTARS

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Summary

The process of underground coal mining cannot proceed safely unless the mine environment is monitored for the range of gases which are injurious to health directly or harbingers of deadly mine fires or explosions. This paper seeks to discuss recent developments in gas monitoring, ranging from new types of portable gas analysers to ultrafast miniature gas chromatographs soon to be trialed in Queensland. Also discussed will be the main parameters which must be considered when purchasing such equipment. Gas monitoring will never be the complete answer to underground coal mine safety but it is an indispensable component of a coal mine protection strategy. There are many exciting gas sensor developments currently being embraced by the mining industry and yet others that we may have to wait for some years to realise.

Introduction

Coal mine atmospheres have been monitored for hundreds of years by a variety of means ranging from Davey Lamps (although they were initially designed for illumination) canaries (sensitive to carbon monoxide and low levels of oxygen) to the plethora of portable and fixed electronic gas devices currently available on the market. The type of device used is only as good as the training provided to the potential operator. The main gases of interest with respect to underground coal mining are carbon monoxide, methane, oxygen, nitrogen, hydrogen sulphide carbon dioxide, oxides of nitrogen, hydrogen and, in some cases, higher hydrocarbons. There is no single gas analyser available which will measure all of the above gases with the degree of accuracy required by the coal mining industry. This means that a range of analysers are required to provide a complete analytical picture to facilitate the identification of spontaneous combustion and for the control of mine fires.

The challenge for coal mines lies in being able to rapidly and accurately measure the gases of interest using robust devices which are reasonably priced and require minimal levels of maintenance. Many of the current range of gas analysers fulfill the accuracy requirements but require intensive levels of maintenance.

This paper explores several significant developments in gas detection methodology that are impinging on the practical world of mine gas monitoring.

To assist in the discussion the major areas of development can be divided into three categories, gas chromatography, sensor technology, and information technology advances.

The last of these three will be seen to be having a major impact on the functionality of the gas chromatography and sensor systems.

Gas Chromatography

Gas chromatographs have been an analytical feature of the Queensland coal industry since the late 1980's and the Computer Assisted Mine Gas Analysis System (CAMGAS) system now covers every major underground coal mine in Queensland and one site in NSW.

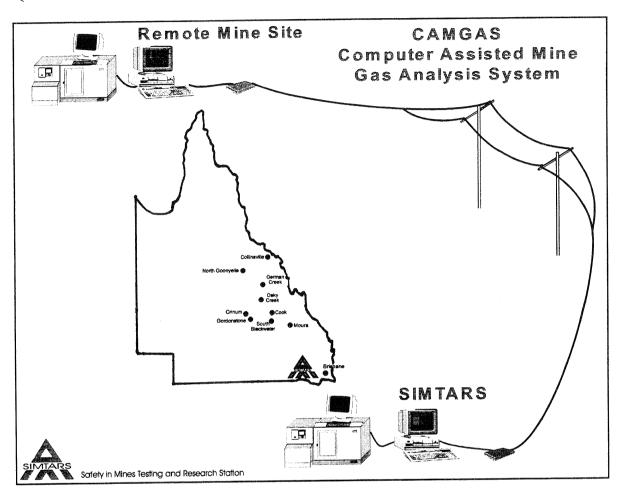


Figure 1. CAMGAS Locations

CAMGAS provides an accurate analysis of all the mine gases of interest with the exception of oxides of nitrogen and hydrogen sulphide. The analysis time of 20 minutes and the cost of the system (\$60,000) are areas in which we can seek significant improvements. In the event of a mine fire or explosion an analysis time of even 20 minutes can be a major problem.

Research and development in the United States associated with the space program and, in particular, with the dispatch of spacecraft to Mars with lightweight gas chromatographs (M200 MTI Ultrafast Gas Chromatograph) has led to the production of a high speed micro gas chromatograph. To survive the rigours of space and to function in harsh environments these devices had to be robust, highly accurate and have low power and carrier gas requirements.

Small portable gas chromatographs have been developed in the past and indeed SIMTARS has several (AID and Baseline) but these units use standard packed column technology with the concomitant delay and never achieved the low levels of sensitivity for carbon monoxide and hydrogen required for predictive mine fire or explosion work.

The new micro gas chromatographs are constructed utilising the same batch fabrication and chemical etching technology used in the semiconductor industry to miniaturise all of the components of a normal gas chromatograph resulting in a chromatography module not much larger than a pack of cigarettes. The whole unit including power supply and on board gas supply providing up to 20 hours of use fits into an instrument unit not much larger than a shoebox. Up to four independently controlled GC modules can be included in each device. This means that each unit could conduct four different chromatographic separations simultaneously.

The main benefits for the coal mine user are as follows:

1. Extremely Fast Analysis Times.

A typical mine gas analysis now taking 20 minutes or longer can be completed in less than 70 seconds. A complex natural gas analysis which can take up to 1 hour on a normal gas chromatograph can be completed in two minutes. These times are not far behind the response time of infra red analysers and can therefore provide almost continuous monitoring. This means much faster analysis in mine emergency situations where every second counts.

2. Rugged, Portable Units Capable of Use in Remote Locations.

SIMTARS after an assessment period would propose to use this unit in the new mobile gas analysis facility to be run by SIMTARS in conjunction with the Queensland Mines Rescue Service. The utility of the small size and robustness have been proved by its initial deep space use.

3. Analytical Accuracy

The ultrafast GC offers accuracy comparable to our current systems but with more definitive identification as a result of having up to four separate chromatographs in the one unit. This enables confirmatory analysis of rogue peaks such as helium to be easily accomplished. The integrator system included with the chromatograph is Windows-based and can provide a comprehensive data collection and analysis facility compatible with the SIMTARS SPLUS system. The interface also makes the system suitable for remote diagnostics such as that available through the CAMGAS network.

4. Cost

Current units sell in Australia for approximately \$40,000 including the computer and data handling system. This is significantly cheaper than a comparable normal sized GC system.

5. Low Power and Gas Requirements

The small size of the unit and low volume of the chromatographic voids means that power and carrier gas usage are extremely low. The gas chromatograph can operate for up to 20 hours on its own power and gas supplies. This means that transportation to a remote mine site could be achieved without turning the unit off.

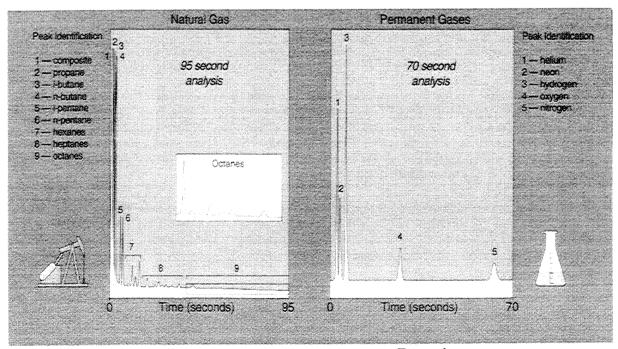


Figure 2. MTI Chromatograms - Examples

SIMTARS will be trialing an M200 MTI Ultrafast GC over the next six months and will subject it to the full range of gas analysis scenarios expected at a coal mine in normal and fire explosion situations. CSIRO at Lucas Heights in Sydney have been conducting similar trials on an MT200 analysing gas from refuse dumps. Over 1000 samples have been analysed with minimal problems and it should be borne in mind that refuse gas streams contain mercaptans and numerous other toxic gases which are normally not tolerated well by gas chromatographs. The early indications are that the MTI Gas Chromatograph will be suitable for coal mine applications.

Sensor Technologies

A wide array of sensor types are utilised in both fixed and portable monitors in the pursuance of complete and accurate gas analyses. These include the faithful infrared sensors used in tube bundle monitoring systems as well as the electrochemical/electro-catalytic sensors routinely used in remote sensor systems and portable monitors. But the further development of these sensors has not stopped even though they have gained acceptance at their current levels of performance.

Alternative sensor technologies which may in the future present real competition for these accepted sensor types are also striding down the development road.

Electro-Catalytic Sensors (Pellistors) (Flammable Gases)

Pellistor type methane sensors currently used in underground fixed systems and in most portable flammable gas monitors have significant problems with respect to zero drift, fall off in sensitivity, frequent servicing and high maintenance costs. The mechanism relies on the oxidation of flammable gas on a catalyst coated coil of platinum wire. At high concentrations due to lack of oxygen the signal decrease and becomes unreliable. This type of sensor is also subject to poisoning by various compounds such as lead, sulphur, silicones, and halogenated hydrocarbons.

As a result much of the research into improving pellistor capabilities is aimed at the development of catalyst coatings that are resistant to poisoning. Materials research is succeeding in this venture and modern instruments exhibit significant resistance to attack, particularly from chemicals likely to be encountered in the coal mining environment.

The efficiency of operating pellistor type sensors or portable gas monitoring units containing pellistors depends on the implementation of a reliable maintenance and calibration program. This procedure still offers only a limited guarantee of accuracy and where critical situations need to be monitored several sensors may be used to monitor a particular location. The majority of currently available combustible gas monitors utilise this type of technology.

Infra Red Gas Sensors (CO, CO₂, CH₄)

The most common format has been to utilise the differential absorption between two specific wavelengths, one not absorbed by the gas of interest while the other wavelength is matched to the absorption characteristic of the target gas. This technique minimises cross sensitivity due to dust and humidity. In some circumstances this method, considered to be of low cross sensitivity suffered from cross sensitivity through indiscrete wavelength selection, and target and non-target species having overlapping absorptions. Improvements in wavelength filtering technology are at the forefront of efforts to reduce cross sensitivities even further.

Developments in interference management have produced a range of modern carbon monoxide monitors that exhibit almost interference free measurement. The modern instrument passes the infrared beam alternately through one cell containing the target gas and another with the target gas catalytically removed. The two signals are then passed through an interference filter prior to comparison by software . This effectively cancels out interfering gases and provides excellent zero and span stability.

The optics required in infrared instruments has long confined their use to fixed installations or to exist as cumbersome and somewhat fragile portable monitors. But that is changing with recent efforts exploiting rugged miniaturised optics which allow adequate sensitivity with great selectivity from instruments small enough to take the place of an electrochemical cell in a hand held-monitor. The development of reflected ray passages has increased the path lengths achievable in compact instruments and has promoted their usefulness as fixed sensors and portable monitors.

Currently these sensors are effectively applied to the selective measurement of methane or carbon dioxide, and within a few years it is anticipated that the development of a cell sensitive enough to measure carbon monoxide in ppm quantities will become a reality.

Indications are that light emitting diode sourced liquid crystal based devices are being developed to become competitive in terms of costing and sensitivity although they may yet be five to ten years away.

Electrochemical Sensors (CO, O2, H2S, SO2, NO, NO2, HCN, HCl, NH3)

An enormous and increasing range of these types of sensors is available. The most common in use in coal mines is the carbon monoxide detector where carbon monoxide is oxidised to carbon dioxide and the resulting electrical signal is related to the original concentration of carbon monoxide. They tend to have a small dynamic range and are non-linear at high concentrations but they have a fairly low drift and are reasonably inexpensive. They are available for most of the common gases of interest.

Much effort is currently being spent in the reduction of cross sensitivities to which such sensors can be prone. They are also constantly being reduced in size and are now available in instruments capable of carrying five or more sensors in the one unit.

An important advance is the development of "smart sensors" which carry sensor calibration information within the sensor itself. This allows the sensor to be held as a "hot spare" for immediate installation should a similar unit fail in service. Such sensors may be interchanged with other "smart sensors" having different target gases. This allows a single instrument to be reconfigured for the analysis of a different gas array. It also means that instruments need not be sent for calibration in their entirety. Only the spent sensor need be transported while the instrument could remain in service using "hot spares".

Information Technology

Many of the advances in sensor technology involve interfacing information technologies to the existing sensor systems. In many cases this has resulted in a broadening of the functionality of system and improvements in analytical traceability.

Information technology promoted the development of the CAMGAS chromatography system that popularised chromatographic techniques under conditions where maintenance of such equipment had regularly failed.

The continued improvements in modem communications software have further permitted the development of remote access instrumentation which allows immediate diagnostic capabilities and true "on-line" assistance for the minesite CAMGAS user.

These advances promote the possibility of sophisticated gas analysis equipment being maintained on-site with the assistance of skilled personnel provided by a central agency. Such equipment can include hybrid tube bundle/sensor systems, fixed gas monitors, remote sensors or gas chromatographs. Increasingly one does not need to be on-site to diagnose equipment faults or to provide maintenance.

Portable monitors have changed from simple safety lamp replacements to sophisticated data recording stations with the capability to store information on four or five gases for the duration of a shift. Later they can present this information in graphical and tabular form complete with documentation of any warning level excursions. It is worth mentioning again that modern sensors can carry calibration information within the sensor for immediate replacement (above ground) should a similar unit fail in service.

Increasingly the microcircuitry available within sensors is being utilised to improve the characteristics of the measurement provided. Outputs are linearised, cross sensitivities are compensated for, and intelligent sensors are instructed when to allow a sensor of more suitable dynamic range to take over, all through the use of improved logic circuits. It is certain that we have not seen the limit of ingenuity with regard to this.

Future Directions

Large investments are being directed into sensor technologies and significant improvements are being made not only to the miniaturisation of instruments, but as importantly, also in their functionality. When the practical considerations are made prior to purchasing gas sensing equipment, today or in the future, the following issues are paramount and are the areas into which the majority of resources are being channelled:

- a. Sensitivity
- b. Interferences and cross sensitivity
- c. Robustness
- d. Ease of use
- e. Data handling

Regardless of the advances in technology yet to be made these criteria will remain necessary components of a successful gas monitoring system. End users of the equipment should also add service and spare parts availability as important criteria.

Portable instruments now provide reliable measurement and recording of target gases in most matrices encountered underground, and other sensors whether infrared or electrochemical, have been developed to provide stable, selective gas monitoring in all but the most difficult of atmospheres.

Improved chemical sensors linked in arrays and associated with computerised information handling may offer improved selectivity and sensitivity and could ultimately develop into instruments approaching the ideal.

What remains is the prospect of developing a single device that is capable of providing a direct reading of complex mixtures of gases including those existing prior to, during, and after a mine fire.

References

- 1. Kochan, A. "Sensor Research at the French Atomic Energy Commission", Sensor Review, Vol 16, No.2, 1996, p38-40.
- 2. Eilmes, C. "Polytron 2 A New Generation of Stationary Gas Measuring Heads", Drager Review, Vol 74, Jan 1995.
- 3. Bendisch, G. And Diekmann, W. "Polytron IR Ex A Stationary IR Measuring Head for Flammable Gases and Vapours", Drager Review, Vol 72, Dec. 1993.
- 4. Wright, J. D. "Chemical Sensor Past, Present and Future", Chemistry in Britain, 1995.
- 5. Van Ewyk, Dr R. "Flammable Gas Sensors and Sensing", Measurement and Control, Vol 29, Feb 1996.
- 6. Walsh, Dr. P. "Toxic Gas Sensing for the Workplace", Measurement and Control, Vol 29, Feb 1996.
- 7. Baines, T. and Mabbitt, A. "A Leading Light in Gas Detection", Process Engineering, Jan 1996.