# Low temperature volatile organic profile of Australian coals


## Fiona Clarkson[1], Daniel Usher[2]

Research Scientist, Simtars[1]
Analytical Chemist, Simtars[2]



#### Abstract

The low temperature volatile organic profile of coals from the Bowen Basin and Upper Hunter Region was investigated to identify the presence of compounds that would allow mines to better identify the onset of a heating and monitor its progress.

Before new methods and techniques could be developed for use in conjunction with current monitoring systems it was necessary to gain an understanding of the range of volatile compounds that may be present from low temperature heating of coal. A series of small, medium and large scale test were undertaken to confirm the presence of aromatic, branched chain hydrocarbons and carbonyl species in high to low rank Australian coals undergoing potential spontaneous combustion.

It was found that there were three series of compounds that could be used as indicators of coal temperature for both Bowen Basin and Upper Hunter coals. BTEX(benzene, toluene, ethyl benzene and xylene)/trimethyl benzene, alkane and carbonyl based profiles were identified that indicated minimum coal temperatures of 60ºC and 80 – 100ºC.

A series of mine specific aromatic hydrocarbon, alkane and acetaldehyde based ratios were also derived for use in identifying the onset of a heating.

The limitations of using these findings in the current mining environment will also be discussed.


#### Introduction

Oxidation of coal leading to the generation of heat is a natural consequence of the weathering of coal. The coal temperature will increase if this heat cannot be dissipated and a spontaneous combustion event may result if there is sufficient heat accumulation. In a review of spontaneous combustion incidents between 1972 and 2004, Ham (2005) identified 51 incidents of spontaneous combustion in Queensland mines and a further 36 in the Newcastle and Hunter Regions of New South Wales (NSW). In the underground mining environment these events have been and continue to be a serious threat to safety and productivity. During the period 1972 to 1994, forty-two Queensland miners were lost due to spontaneous combustion incidents (Cliff, Rowlands and Sleeman, 1996) As recently as 2003 a longwall goaf fire in the Southland Colliery, (Ham, 2005) resulted in the mine being sealed.

Constant monitoring for spontaneous combustion and implementation of remedial measures as soon as possible after the identification of its occurrence are therefore vital to the well being of a mine. Trending of carbon monoxide (CO), hydrogen, ethylene and $CO/CO_2$ ratio (carbon monoxide/carbon dioxide ratio) together with Graham's ratio and CO make which are independent of air flow are among the commonly used indicators of spontaneous combustion in Australian mines. (Cliff 2005) However these indicators may be limited in their ability to provide early detection of a heating and it has been shown in some cases that the trigger levels set at the mine are exceeded only in a large scale heating or when the heating is too advanced to treat. (Humphreys 2004) Not withstanding these limitations, the trending of these indicators can be used to indicate if a heating is deteriorating or improving and can be used to monitor the effects of remediation techniques. (Cliff et al, 2000, Cliff 2005)

Simtars has undertaken a series of research projects in an attempt to gain a better understanding of spontaneous combustion and to develop new methods and techniques to monitor spontaneous combustion. One of the research projects, ACARP Project C5031 (Cliff et al, 2000) identified the presence of aromatic, aliphatic, chlorinated and oxygenated hydrocarbons in the off-gases from Moura coal at temperatures above 100°C. The presence of some aromatic and oxygenated species below 100°C was also indicated leading to the possibility of determining a temperature range and profile for these compounds as these compounds could potentially be integrated into the *fire ladder (*Cliff et al, 1994).

A 1985 review by Hurst and Jones of overseas investigations into the low temperature heating of coals had also identified a series of organic components as present including alcohols, aldehydes, ketones, alkanes and aromatic hydrocarbons. A further gas chromatography – mass spectrometry (GC-MS) study on a UK coal by Hurst et al. (1985) identified benzene, methyl cyclohexane, toluene and xylene as present between 70°C and 90°C.

The Simtars research project, ACARP Project C10015 (Clarkson 2004) investigated the profile of aromatic and aliphatic compounds in a New South Wales coal using a fast gas chromatograph (fast GC) with a piezoelectric sensor unit. The instrument while limited in its usefulness below 100°C was able to discriminate as to whether a heating was at an advanced stage or not. Analysis of the off-gases by GC-MS identified the presence of a number of alkanes, aromatic and oxygenated compounds for the NSW coal reacting below 100°C.

The interim C10015 Report stated that, *A better understanding of the range of volatile compounds that are or are not present from low temperature coal heating is required. This together with a knowledge of the compounds routinely found in the mine atmosphere will determine if electronic noses or even other analytical techniques can be applied to the detection of a low temperature heating.* (Clarkson 2004)

This body of information was the basis for the extension to ACARP Project C10015 *Detection of Heating of Coal at Low Temperatures*, (Clarkson, Kelly, Usher, Van Rijn, 2007) the results of which are reported here.

## Experimental

### Small scale testing

A low rank Queensland coal was step heated from 50 °C to 110 °C in Simtars' small scale gas evolution apparatus. The off-gases were collected on ATD, SKC 226-119 and SKC 226-51 tubes. The nominal sample volume was 1.5 litres. The ATD (automated thermal desorption) tubes were used to collect samples for later GC-MS analysis to screen for the presence of aromatic, straight and branched chain hydrocarbons. SKC 226-19 tubes were used to collect samples for high performance liquid chromatography (HPLC) analysis to screen for the presence of oxygenated compounds (carbonyl compounds). SKC 226-51 tubes were used to collect samples for gas chromatography – flame ionisation detector (GC-FID) screening for the presence of methanol. Full details of the apparatus, flow rates and sampling times for testing are reported in Clarkson et al. (2007).

### Medium Scale test reactor

The two metre column used in this testing is the second of two built by the University of Queensland and was loaned to Simtars for use in ACARP Project C10015 Extension to Detection of heating of coal at low temperatures.

The basic operation of the column was described by Beamish et al. 2002 and Hancock et al. (2005) The column (Figure 1) is divided into eight sections each with a thermocouple in the wall and the core, an independent heating element and a gas extraction port. The column is insulated and each section can be heated individually. Simtars configured the column with a plenum chamber at each end by inserting mesh grates 255 mm from each end. Each test required approximately 60kg of coal depending on the packing density. The column was operated in the horizontal position rather than vertically. For the testing undertaken the column was operated in step mode with the heater units used to raise the coal temperature to a predetermined point prior to collection of gas samples for analysis.

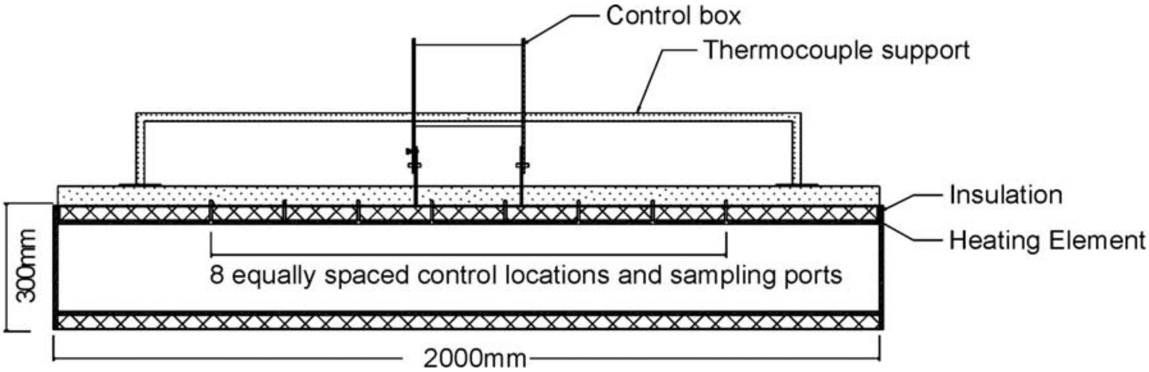


Figure 1 Diagrammatic representation of University of Queensland 2m column

Two coals of varying rank from Queensland and one from NSW were used in the tests. The tests involved heating the coal sample while passing instrument air at 0.5-0.6L/min through the column. VOCs, oxygenated compounds (carbonyl compounds) and methanol were sampled from the exhaust and various ports along the column dependant on the temperature profile of the core during each analysis event. A water trap was placed in the line before the ATD, SKC 226-119 and SKC 226-51 sorbent tubes to condense moisture in the sampling line. For the lower rank coal samples, the dropout tube was placed in an ice bath to increase the ability to condense moisture in the lines. The nominal sample volume was 5 litres. Full details of the flow rates and sampling times for each test are reported in Clarkson et al. 2007.

In addition, gas samples were collected in aluminium bags from the specific ports at each temperature step. Mine gas analysis: consisting of determination of oxygen, carbon monoxide, carbon dioxide, hydrogen, methane, ethylene, ethane and nitrogen was carried out on these samples according to Simtars method LP0043 - *Procedure for Analysis of General Permanent Gases Using a Micro Gas Chromatograph (*Simtars 2007a). Where indicated samples were also collected in Tedlar bags for analysis of the higher alkanes according to Simtars method LP0023 - *Procedure for Analysis of Natural Gas using a Micro Gas Chromatograph* (Simtars 2000b).

**Large Scale test reactor**

The full details of Simtars' 16m3 reactor are described in Clarkson (2005). The reactor holds 15 to 18 tonnes of run of mine coal in a pile 2m high, 2m wide and 4m long. A thermal cover and heated recirculated air system are used to control the reactor temperature. The temperature of the coal is monitored via 5 layers of 50 thermocouples embedded in the coal, with a 0.4m spacing between each thermocouple. Gas samples are drawn from the reactor via sixteen gas sampling tubes inserted into and across the central axis of the reactor and also the exhaust gas outlet.

**Results and Discussion**

**Small Scale testing**

The small scale testing of the off-gases from a low rank Queensland coal, QLD – C1, confirmed the presence of xylene and the alkanes (n-hexane to n-decane) below 100°C. Trimethyl benzene, chlorinated compounds, ethyl acetate and 2-butoxyethanol were not consistently detected in the small scale instrument air tests.

The presence of a number of aldehydes including acetaldehyde, acrolein/acetone and propionaldehyde was also confirmed below 100°C. The concentration of the individual alkanes and aldehydes was found to increase with temperature.

### Medium Scale testing

### High rank Queensland coal test

The high rank coal, German Creek 10, from the Bowen Basin was sampled from behind a continuous miner and sealed into buckets. The sample was heated in a series of steps from 30°C to 120°C. The heating profile immediately prior to sampling for the hydrocarbon and carbonyl compounds shows the development of a localised heating at Port 7 for a nominal column temperature of 100°C. See Figure 2 The generation of a hot spot near the inlet of the column is indicative of the occurrence of spontaneous combustion event in the 2m column.

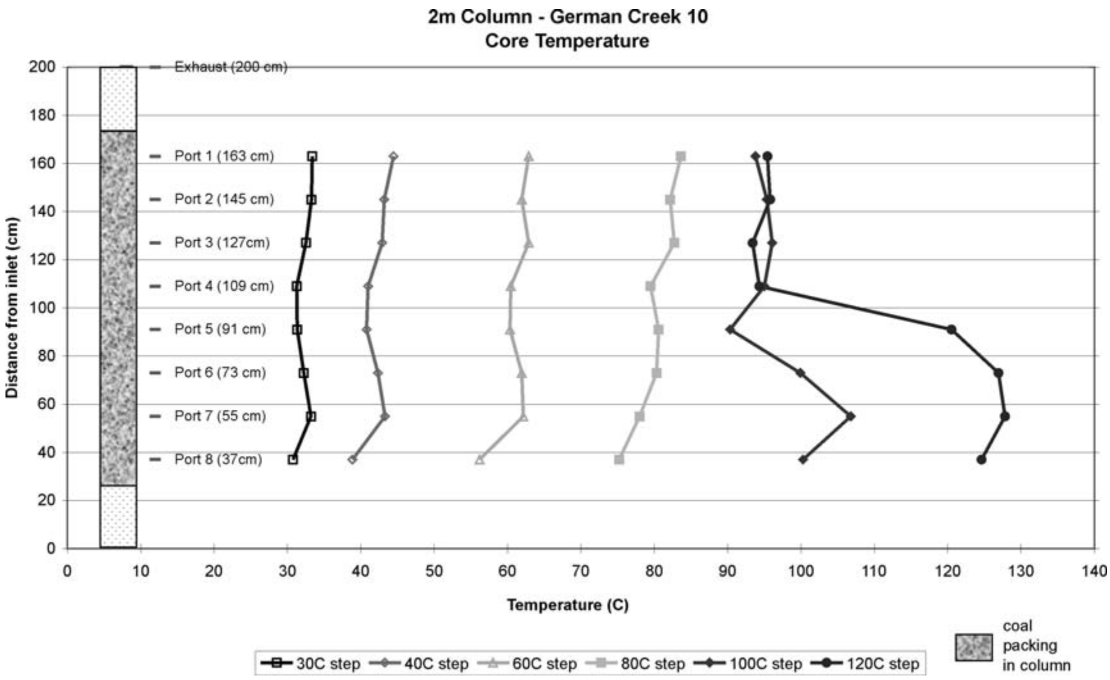


Figure 2 German Creek 10 temperature profile

Samples were collected initially from the exhaust and Port 5 and subsequently the exhaust and Port 7 following the development there of the localised heating. The exhaust gases at a nominal coal temperature of 80°C were found to contain benzene, toluene, xylene and trimethyl benzene. Ethyl benzene was not detected until the maximum measured coal temperature exceeded 109°C. Benzene (62ºC), toluene(42ºC) and xylene(62ºC), were found at lower coal temperatures in gas samples drawn from Port 5 which was downstream from the site where the heating later developed. Once detected at a port of interest, the concentrations of the aromatic compounds increased with increasing coal temperature.

The BTEX compounds together with trimethyl benzene form a profile (fingerprint) which could be used to indicate a minimum coal temperature.

Methyl cyclohexane and n-heptane were found to be present in the exhaust gases from 40ºC with the higher alkanes n-octane, n-nonane and n-decane present once the maximum coal temperature exceeded

64ºC. These compounds appeared in the same sequence in Port 5 but not until the next 20ºC temperature step had been completed compared to the exhaust appearance temperature.

The carbonyl profile of the coal off-gases was also investigated at the same time. The most abundant aldehyde identified from the exhaust and Port 5 off-gases was found to be acetaldehyde. This aldehyde together with a component comprising either acrolein and or acetone was present from a nominal coal temperature of 30ºC. Although the sampling and analysis was not repeated for the German Creek 10 sample, it is likely that the component identified as "acrolein / acetone" consisted of acrolein only. The initial aldehyde analysis method was not able to separate acrolein and acetone. However an analysis method subsequently available and used on all further aldehyde testing on the project could separate these two components. No acetone was found to be present in the other Bowen Basin or Hunter coals test.

The acetaldehyde and acrolein concentrations were observed to increase significantly between 60 ºC and 80ºC. At the same time the aldehyde profile became more complex with propionaldehyde present in all sampled ports from 80ºC onwards. The exhaust gases at this temperature also contained methyl ethyl ketone (MEK) and butyraldehyde. Formaldehyde was present in all sampled ports from 120ºC as was hexaldehyde.

**Medium rank coal test**

A medium rank coal sample, Northern Bowen Basin 42 was used for this investigation. The coal sample came from a longwall panel and had been immersed in water and sealed into buckets for shipment. Immediately prior to testing, the sample was air dried so that the moisture content would approximate that of an as received mine sample.

The heating in the Northern Bowen Basin 42 sample developed around Ports 6 and 7. Gas samples were collected from the exhaust and Ports 4 and 7.

While toluene was found to be present at temperatures as low 30°C - 40°C in the reactor off-gases, benzene, toluene, and xylene were identified in all ports from 60°C onwards which is 20°C lower than the German Creek 10 profile. The appearance temperature for ethyl benzene was also lowered approximately 20°C compared to the high rank sample, being detected for coal temperatures of 80 to 90°C. Trimethyl benzene was present in all ports from 100°C but was also present in the exhaust gases from 80°C.

Methylcyclohexane and n-heptane were present in the 30ºC to 40ºC range in the Port 4, 7 and exhaust off-gases compared to 60ºC and 40ºC respectively for the high rank coal sample. The expanded VOC screen also confirmed the presence of n-hexane from 40ºC. The higher alkanes had a similar appearance temperature to that found for the high rank coal sample.

Further investigation of the lower alkane profile (propane, iso-butane, n-butane, neo-pentane, iso-pentane, n-pentane or n-hexane) using a micro GC configured for natural gas analysis proved inconclusive as the reporting limit for these components is 100 ppm (0.01 vol%). This is significantly larger than the highest reported hexane level of ~1.5ppm for the medium rank coal sample being investigated.

The aldehyde testing confirmed the presence of acetaldehyde and acrolein at temperatures as low as 30ºC in the medium rank coal. Propionaldehyde was also present at 30ºC indicating that its appearance temperature may be coal rank dependent. Significant increases in the acetaldehyde (10 times) and acrolein (4 times) concentrations were again observed for nominal coal temperatures of 60ºC and 80ºC. Propionaldehyde also exhibited a 10 fold increase in concentration between 60ºC and 80ºC. From 80ºC onwards the aldehyde profile became more complex with butyraldehyde, isovaleraldehyde, valeraldehyde and hexaldehyde present. Formaldehyde was present in all ports sampled from 100ºC to 120ºC.

**Low rank coal test**

The low rank coal, Upper Hunter 6, from New South Wales was sampled underground and sealed into buckets. The sample was heated in a series of steps from 25°C to 120°C as the insitu rock temperature in New South Wales is lower than in Queensland. The heating profile immediately prior to sampling for the hydrocarbon and carbonyl compounds showed the development of a localised heating at Port 6 which migrated towards the inlet in the final stages of the test.

Toluene was present from 26ºC and together with benzene was present in all sampled ports from a nominal coal temperature of 60ºC. In contrast to the medium rank coal, xylene was not present within the coal pile until approximately 80ºC nor in the exhaust gases until the majority of the coal exceeded 90ºC. Ethyl benzene and trimethyl benzene were present in the exhaust gases for coal temperatures of 85 to 100ºC.

The alkanes n- hexane (26ºC), n-heptane (26ºC), n-octane (60ºC) and n-decane (0ºC) were found to appear in a similar temperature range to that already seen for the medium rank sample. The remaining alkanes, methyl cyclohexane (40ºC - 60ºC) and n-nonane (80ºC), were not present in the low rank NSW coal until higher coal temperatures compared to that identified for the for the medium rank Queensland coal sample.

The aldehyde testing confirmed the presence of acetaldehyde and acrolein at temperatures as low as 26ºC in the low rank coal while propionaldehyde was not present until 60ºC. As had been found in the Queensland coals significant increases in the acetaldehyde, acrolein and propionaldehyde concentrations were observed for nominal coal temperatures of 60ºC and 80ºC (Figure 3). From 60ºC onwards the aldehyde profile became more complex with butyraldehyde and formaldehyde also present.

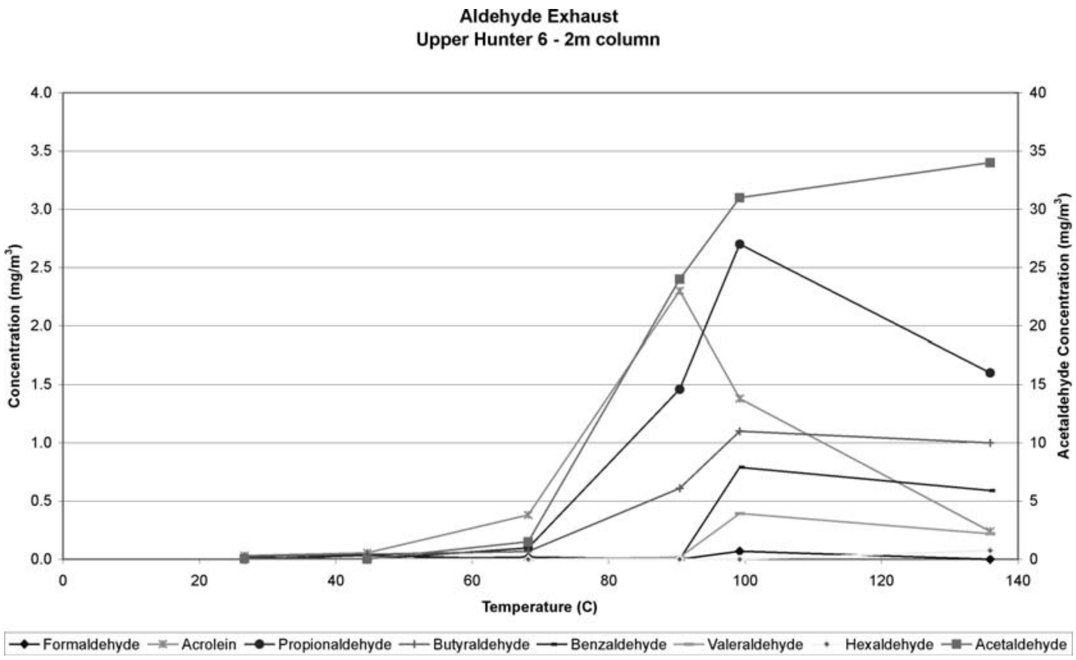


Figure 3 Upper Hunter 6 aldehyde profile

A series of ratios were calculated based on the major component in the BTEX/trimethyl benzene, alkane and aldehyde series (toluene, heptane and acetaldehyde) in order to remove concentration dependence as a factor. The results showed that while there may be a VOC based trend for an individual mine, the same ratio may not be as effective in another mine even in the same coal basin eg. the trimethyl benzene/toluene ratio clearly increases with temperature for German Creek 10 however the same ratio for the Northern Bowen Basin 42 sample increases at approximately one tenth the rate (Figure 4).

The Northern Bowen Basin 42 sample also exhibited a clear trend for a heptane based ratio which is not apparent for the German Creek 10 sample. The New South Wales coal Upper Hunter 6 did not exhibit a clear trend for either a toluene or heptane based ratio.

All three coals do however show a trend with temperature for an acetaldehyde/acrolein based ratio (Figure 5). Formaldehyde, propionaldehyde, crotonaldehyde and butyraldehyde also appear to have potential in some cases for use in an aldehyde/acetaldehyde ratio or acetaldehyde/aldehyde ratio.

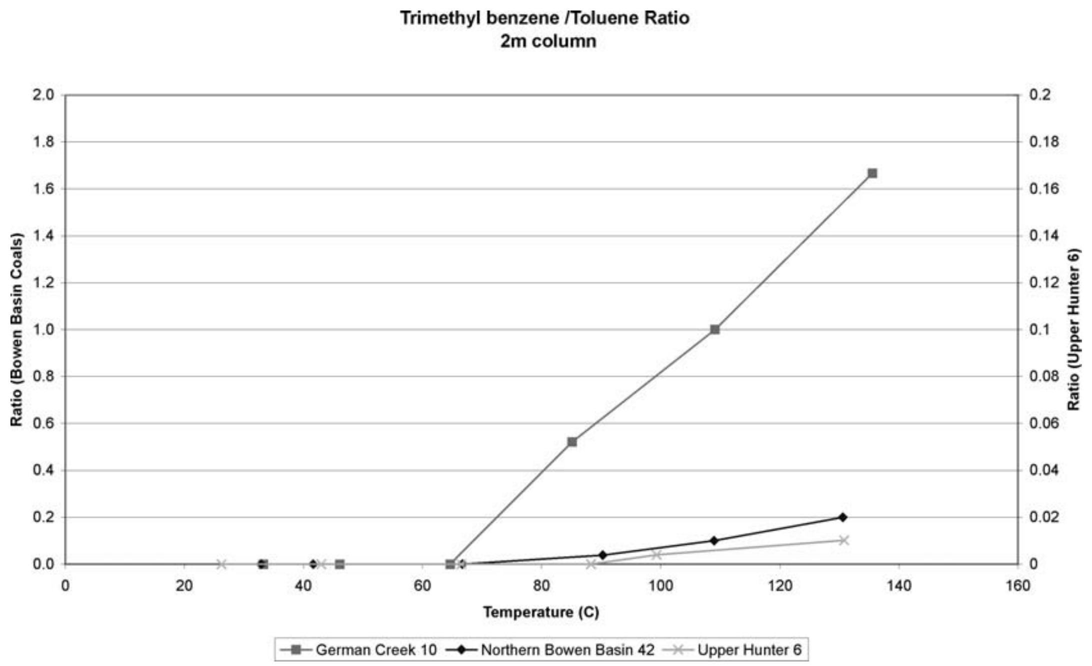


Figure 4 Trimethyl benzene/toluene ratio

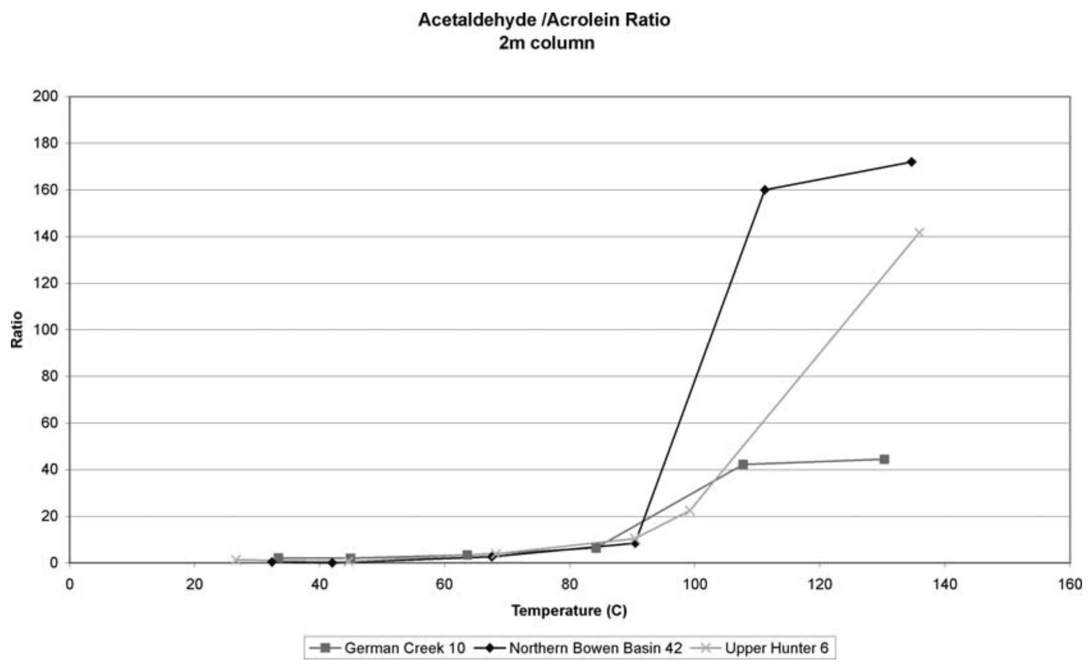


Figure 5 Acetaldehyde/acrolein ratio

**Large scale testing**

The low rank QLD - C1 coal was allowed to self heat and achieved a maximum coal temperature of 73.9°C before the test was shut down.

The VOC fingerprint for the QLD - C1 coal sample was complex with respect to the BTEX/Trimethyl benzene components as was found in the 2m column tests for a low rank coal sampled at 50ºC or higher. Octane was not present in the reactor until the coal temperature was between 57ºC and 60ºC. At 60ºC or above n-octane was consistently found in the gas samples which corresponds well with the findings from the 2m column work.

In the case of the aldehyde fingerprint, the aldehyde components do not exhibit a clear trend which can be compared with the 2m column testing. However on a qualitative basis propionaldehyde is only observed in samples collected when the 16m3 reactor temperature was greater than 58ºC which correlates with the 2m column results where propionaldehyde was consistently observed for temperatures of 60ºC or greater.

The concentration of acrolein was also consistently higher than that of the other aldehydes reported from the large scale16m3 test.

In applying these findings to the current mining environment there are a number of factors that will need to be taken into account.

- Sampling for the aromatic and aliphatic (alkane) components identified here will require the use of ATD tubes (ppb range) rather than stain tubes (ppm range).
- General body dilution may make detecting the compounds of interest especially BTEX / Trimethyl benzene difficult. The most appropriate places to monitor in a mine have yet to be identified.
- Large sample volumes will be required to improve the Limit of Detection (LOD).
- The aldehyde sorbent tubes must be kept frozen prior to use. After sampling both the aldehyde and ATD tubes must be kept chilled and then analysed within a few weeks of collection for sample stability.
- Real time / mine site analysis is not currently possible due to the analytical instrumentation required. Turn around times could be a minimum of several weeks due to transportation time and batch processing of samples. This time frame may not be short enough for the mine to meaningfully utilise the results of the analyses.
- The BTEX, trimethyl benzene and alkane components and some of the aldehyde components identified in the coal fingerprint are also present in the diesel fingerprint although in different ratios.
- The presence of an unknown compound was detected in the Northern Bowen Basin 42 and Upper Hunter 6 aldehyde samples. This compound is thought to be ozone, which reduces the capacity of the DNPH sampler to absorb aldehyde. A potassium iodide (KI) denuder will need to be placed in front of the aldehyde sampling tube if the presence of ozone is confirmed or known to exist in the sampling environment.

Not withstanding these limitations, the VOC profile is of potential use in estimating the coal temperature.

- The information can be used both quantitatively and also qualitatively, analogous to mine practice now for the standard mine gases.
- Individual components eg toluene, benzene, xylene, n-hexane, n-heptane, n-octane, acetaldehyde, acrolein, propionaldehyde and butyraldehyde can be trended. The acetaldehyde in particular seems to have a marked temperature response that is at least 20ºC lower than the appearance temperature of ethylene (Figure 6).
- There seems to be appearance temperatures above the normal working temperature of a mine for certain components eg the presence of either propionaldehyde or n-octane indicates the coal temperature is in excess of 60ºC.
- Several potentially useful ratios for trending have been identified eg benzene/toluene, xylene/toluene, trimethyl benzene/toluene, MEK/toluene, MEK/heptane, acetaldehyde/acrolein.

- Not all the components generating useful trends are part of the fingerprint for the diesel vehicle tested eg. Acrolein is absent from the diesel spectrum and acetaldehyde is present in low levels.
- The diesel VOC fingerprint is dominated by benzene whereas toluene is dominant in the coal fingerprint.

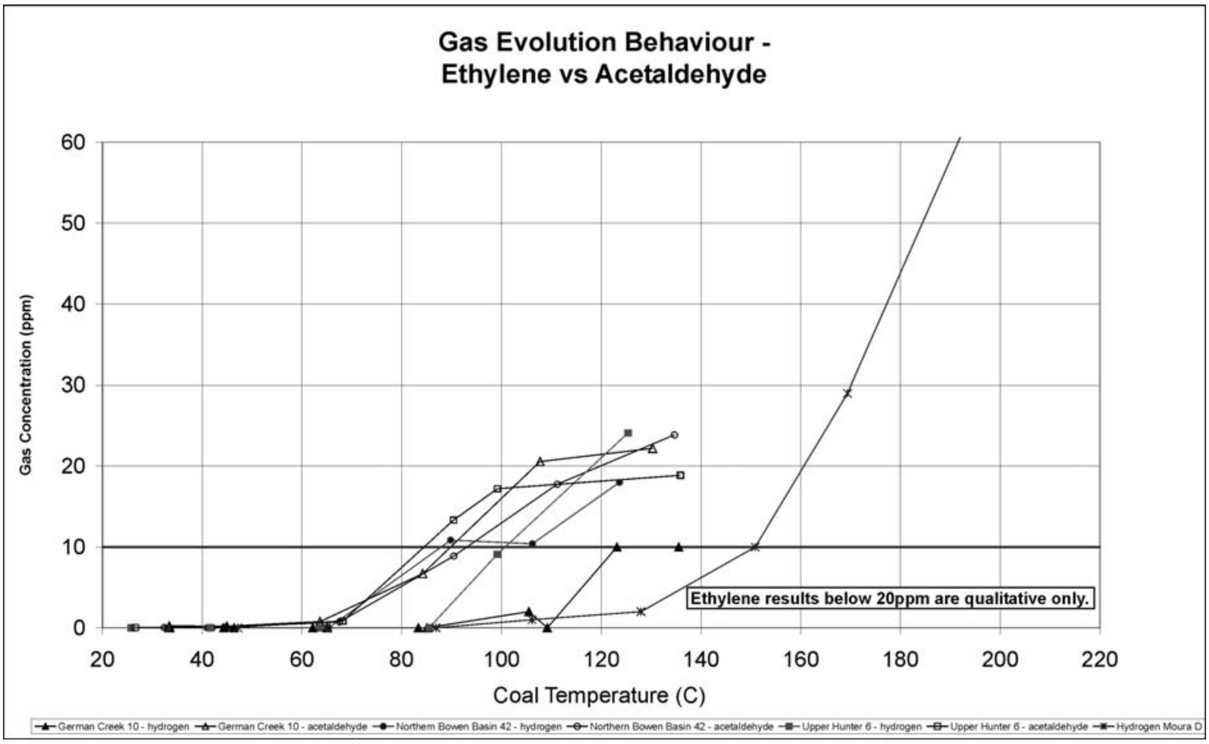


Figure 6  Acetaldehyde and ethylene profiles for three Australian coals

**Conclusions**

The testing confirmed the presence below 100°C of a range of aromatic, aliphatic and aldehyde compounds in the three Australian coals tested.

For the Bowen Basin coals tested several components of a BTEX / trimethyl benzene profile exists from 60 to 80°C with toluene generally observed from 25 or 30°C.  The presence of toluene in combination with benzene and xylene would indicate a minimum coal temperature of 60°C.  If either ethyl benzene or trimethyl benzene were also present then the coal temperature would be expected to be 80 - 100°C.

In the case of the Upper Hunter sample, the presence of toluene and benzene would indicate a minimum coal temperature of 60°C.  If either xylene, ethyl benzene and or trimethyl benzene were also present then the coal temperature would be expected to be 80 - 100°C.

Hexane, heptane and methyl cyclohexane are commonly found below 60°C but at ≥60°C octane and the higher alkanes are progressively observed in the three Australian coals tested.

There is some indication of a rank dependence for the appearance temperature of the aldehyde components.  Acetaldehyde and acrolein are found to be present below 60°C in the three coals.  In the high rank German Creek 10 coal sample and the medium rank Bowen Basin 42 coal a complex aldehyde fingerprint is present from 80°C.  The observed aldehydes increase significantly in concentration from 60°C to 80°C.  Formaldehyde is present from 100°C to 120°C onwards.  In the case of the Upper Hunter 6 coal sample the fingerprint becomes complex from 60°C and includes acetaldehyde, acrolein, propionaldehyde, formaldehyde and butyraldehyde.

## References


Beamish, B B, Lau, A G, Moodie, A L and Vallance, T A, 2002, Assessing the self-heating behaviour of Callide coal using a 2-metre column, Journal of Loss Prevention in the Process Industries, 15:385-390.

Cliff, D I, Bell, S L, Bofinger, C M, Kitchen, B P, 1994. The use of gas analysis to aid in the early detection and monitoring of fires and heatings in underground coal mines, Australian Coal Journal; no.43, pp. 15-23.

Clarkson, F, 2004, Detection of Heating of Coal at Low Temperatures: Interim Report, Australian Coal Association Research Program Project no. C10015, Australian Coal Association Research Program, Brisbane, Qld.

Clarkson, F, 2005, Results of Self-Heating Tests of Australian Coals Conducted in a 16 $m^3$ Reactor, Coal2005 Conference, Brisbane, QLD, 26 - 28 April 2005, p201-208

Clarkson, F, Kelly, T, Usher, D, van Rijn, V, 2007, Extension to Detection of heating of coal at low temperatures, Australian Coal Association Research Program Project no. C10015, Australian Coal Association Research Program, Brisbane, Qld

Cliff, D, 2005, ‘The ability of current gas monitoring techniques to adequately detect spontaneous combustion’, Coal2005: 6th Australasian Coal Operators' Conference: 26 - 28 April 2005, Brisbane, Queensland, AusIMM, Carlton, Vic., pp. 219-223

Cliff, D, Clarkson, F, Davis, R, Bennett, T & Smalley, M, 2000, Better indicators of spontaneous combustion, Australian Coal Association Research Program Project C5031 final report, Australian Coal Association Research Program, Brisbane, Qld.

Cliff, D, Rowlands, D and Sleeman, J, 1996, Spontaneous Combustion in Australian Underground Coal Mines (ed: C Bofinger), (Simtars:Redbank Australia).

Ham, B, 2005, ‘A review of spontaneous combustion incidents’, Coal2005: 6th Australasian Coal Operators' Conference: 26 - 28 April 2005, Brisbane, Queensland, AusIMM, Carlton, Vic., pp. 237-242.

Hancock, M, Kizil, MS &, Beamish, BB, 2005, ‘Computer animation of hot spot development in bulk coal as an aid for training coal miners’, Coal2005: 6th Australasian Coal Operators' Conference: 26 - 28 April 2005, Brisbane, Queensland, AusIMM, Carlton, Vic., pp. 243-248.

Humphreys, DR 2004, The application of numerical modelling to the assessment of the potential for, and the detection of, spontaneous combustion in underground coal mines, PhD Thesis, University of Queensland, School of Engineering Mining Programme.

Hurst, NW & Jones, TA, 1985, ‘A review of products evolved from heated coal, wood and PVC’, Fire and Materials, vol. 9, no. 1, pp. 1-8.

Hurst, NW, Jones, TA, Mann, B, van Ewyk, RL & Walden, P, 1985, ‘Analysis of gases from heated coal, wood and PVC conveyer belt and their effect on zinc oxide single crystal semiconductor gas sensors, Fire and Materials, vol 9, no. 1, pp. 9-22.

Simtars 2007a, ‘Procedure for analysis of general permanent gases using a micro gas chromatograph’, Simtars Procedure LP0043, Simtars, Redbank, Qld.

Simtars 2007b, ‘Procedure for analysis of natural gas using a micro gas chromatograph’, Simtars Procedure LP0023, Simtars, Redbank, Qld.