

2005

# The Use of Electronic Nose Devices for Coal Self-Heating Detection

F. Clarkson

*Simtars, Queensland*

---

## Publication Details

This conference paper was originally published as Clarkson, F, The Use of Electronic Nose Devices for Coal Self-Heating Detection, in Aziz, N (ed), Coal 2005: Coal Operators' Conference, University of Wollongong & the Australasian Institute of Mining and Metallurgy, 2005, 209-218.

# The Use of Electronic Nose Devices for Coal Self-Heating Detection

F Clarkson<sup>1</sup>

## ABSTRACT

Electronic noses are being used in the processing industries and in fields such as environmental and occupational hygiene to detect a wide variety of problems from contaminated foods to toxic chemicals in soils. Recently, research has been conducted into the use of these devices for detecting spontaneous combustion in mines with the aim of producing a method for early detection of a developing heating. Gas samples were collected from both Simtars' 16 m<sup>3</sup> large-scale spontaneous combustion reactor and the University of Queensland's two-metre column. The samples were analysed using an electronic nose. GCMS and HPLC were used to identify some of the components present.

A number of issues both from a practical mine situation and a scientific standpoint have been identified that need to be addressed before these devices can be used to detect a developing heating. Aluminised bags routinely used in the mining industry to collect gas samples for analysis of the permanent gases are not suitable for use with electronic nose devices as they have a 'fingerprint' from the polymer lining that interferes with the coal heating fingerprint. Tedlar bags used for environmental gas sampling are also unsuitable due to their fingerprint. Gas samples can be collected in glass gas bulbs with aluminium seals and successfully analysed. However the aluminium foil used to seal the bulbs is a restricted item in underground mines. It was also found that the volatile organic fingerprint of the coal heating was extremely weak at temperatures below 130°C. Before a useful application can be developed, further investigation into the chemical species present in the off-gases from Australian coals is required.

## INTRODUCTION

A natural consequence of the weathering of coal is that the oxidation process generates heat. If the heat cannot be dissipated, the coal temperature increases leading to an increased rate of oxidation. In instances where there is sufficient heat accumulation, the coal spontaneously combusts and will eventually burst into open fire if there is sufficient oxygen present.

The propensity of coal to spontaneously combust has long been a problem in the mining industry. Available records indicate that in New South Wales from 1960 to 1991 there were one hundred and twenty five incidents of spontaneous combustion reported to the Inspectorate while in Queensland there were 68 reported incidents from 1972 to 1994 (Cliff, Rowlands and Sleeman, 1996). The results of spontaneous combustion episodes even in recent times have had both tragic and serious economic consequences for the mines involved.

Stoppages caused by suspected or actual cases of spontaneous combustion can cause production losses of the order of \$1 000 000 per day. In instances where spontaneous combustion episodes could not be controlled, entire longwall systems have been lost or abandoned. More recently, a spontaneous combustion episode caused an underground fire that resulted in a New South Wales mine being shut down indefinitely and the company placed into liquidation. Loss of life has also resulted from some incidents that could not be controlled. Queensland lost forty-two miners to spontaneous combustion during the period 1972 to 1994 (Cliff, Rowlands and Sleeman, 1996).

The potential to apply electronic nose technology to the problem of the detection of spontaneous combustion has been investigated by Simtars in a series of pilot studies of several commercially available electronic noses and also by several

Japanese researchers who developed an electronic nose based on quartz microbalance sensors coated with a synthetic lipid membrane (Ohga and Higuchi, 1995; Higuchi and Ohga, 1997; Ohga *et al.*, 1999).

Commercially available electronic noses use pattern recognition software to compare the 'fingerprint' or odour profile of volatile compounds to a reference set of odour profiles to identify the unknown odour. The sensing technologies used in these devices includes metal oxide sensors (MOS), metal oxide semiconductor field effect transistors (MOSFET), conducting polymers, polymer composites, quartz microbalance sensors (QMB), surface acoustic wave sensors (SAW), infrared gas sensors and mass spectrometry (Zubritsky, 2000).

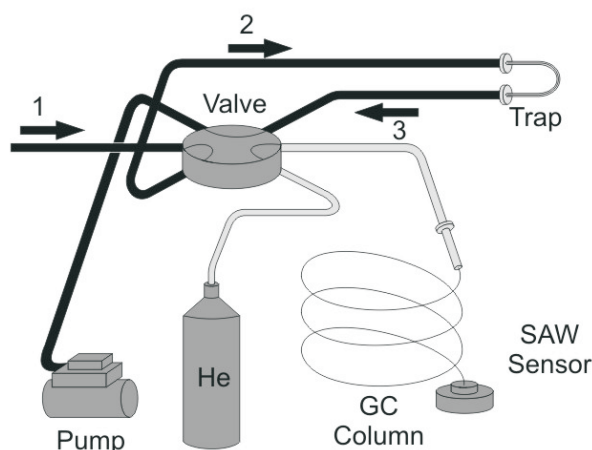
Based on the results of the pilot studies, Simtars undertook to further investigate the use of a commercially available electronic nose to detect spontaneous combustion in ACARP Project C10015 Detection of Heating of Coal at Low Temperatures. The project set out to develop available electronic nose technology and apply it to problems of early spontaneous combustion detection, so that a method could be established whereby mines could identify the onset of a spontaneous combustion, monitor its progress and initiate control strategies.

## EXPERIMENTAL

A run of mine coal sample, NSW-M1, from a Newcastle region mine in New South Wales was obtained for the large-scale 16 m<sup>3</sup> spontaneous combustion test. Details of the 16 m<sup>3</sup> spontaneous combustion test are included in Appendix A of ACARP Project Report C10015 (Clarkson, 2004).

### The zNose 7100 Fast GC Analyser

An Electronic Sensor Technology zNose Fast GC Analyser with a DB5 column and a 'Saw' sensor (Figure 1) was specified for the investigation of the spontaneous combustion heating fingerprint.



Schematic of zNose

FIG 1 - Schematic of zNose in sampling mode.

1. Simtars, PO Box 467, Goodna Qld 4300.  
Email: fiona.clarkson@nrm.qld.gov.au

The operation of the zNose was described by Hester and Clarkson (2003) as follows:

*The Microsensor instrument is a micro-sized automatic thermal desorption gas chromatograph. A gas sample entering the instrument passes through a bed of absorbent material (known as the trap) that collects the analytes of interest. Flash heating of the trap liberates the volatile components onto the separating column in a very narrow band, after which they are separated from one another during the normal traverse of the column. At the end of the column a sophisticated microsensor detects the emergence of separated components from the column. The sensor contains a rapidly oscillating crystal and records the effect that the emerging components have on the oscillating frequency of the crystal while they momentarily adhere to the surface of the crystal. The first differential of the frequency versus time plot provides a reasonably familiar chromatogram.*

As with classical gas chromatographs, the zNose identifies the presence of a particular component based on a characteristic known as the retention time (RT). The retention time is defined as the time at which the detector sees the maximum peak from the emerging component. As each method used to analyse a gas sample represents a unique set of operating conditions, the retention time at which the detector, in this case the microsensor, sees the emerging component was characteristic of that component on that instrument for a particular set of operating conditions.

In the case of the zNose instrument, a series of retention time characteristics of the components of interest were stored in a 'Peak file' linked to the analysis method and used to flag the presence of these components in the gas sample being analysed. The area under the peak was a measure of the quantity of the component adhering to the crystal surface of the sensor and could therefore be used to quantitate the analyte present in the gas sample. The zNose assigned an arbitrary unit of 'Counts' to the area under the peak (equivalent to the sensor's frequency change) unless a scale factor and a defined unit (ie ppm) had been specified.

**Screening tests**

Initial screening tests of the coal gas sampling equipment including aluminised gas sample bags, Tedlar bags and glass gas bulbs were performed using the standard analysis method supplied with the instrument. The method known as 18ps-2.mth was used to determine the suitability of the sampling equipment currently in use in the mining industry and at Simtars for investigation of the coal heating fingerprint (Figures 2 - 4). The coal gas samples used to screen the suitability of the coal gas sampling equipment were obtained from Simtars' small-scale gas evolution apparatus, the 16 m<sup>3</sup> large-scale spontaneous combustion reactor and the University of Queensland (UQ) two-metre column. The 18ps-2.mth method comprised a column ramp rate of 18°C/s and sampling pump duration of five seconds.

**Coal testing – 16 m<sup>3</sup> large-scale spontaneous combustion reactor**

Gas samples drawn from the New South Wales coal sample, NSW-M1, as it was being reacted in the Simtars' 16 m<sup>3</sup> large-scale spontaneous combustion reactor were also analysed using an optimised method R05 s20p20.mth where R05 defines the column ramp rate as 5°C per seconds, s20 defines the sensor temperature as 20°C and p20 was a sample pump duration of 20 seconds. This method also involved the use of a glass

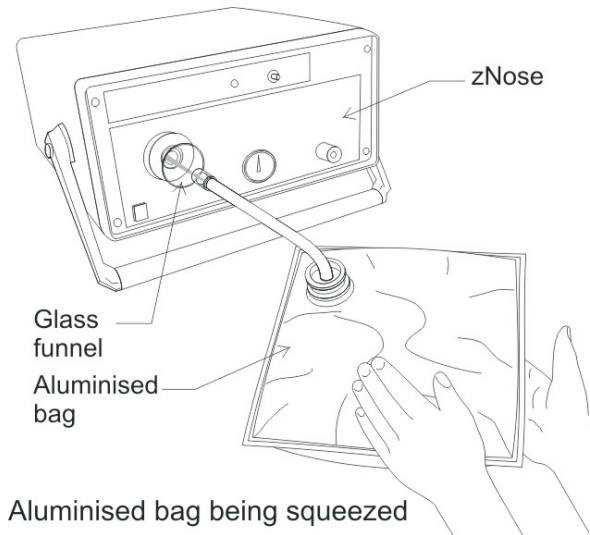


FIG 2 - Sampling from an aluminised bag.

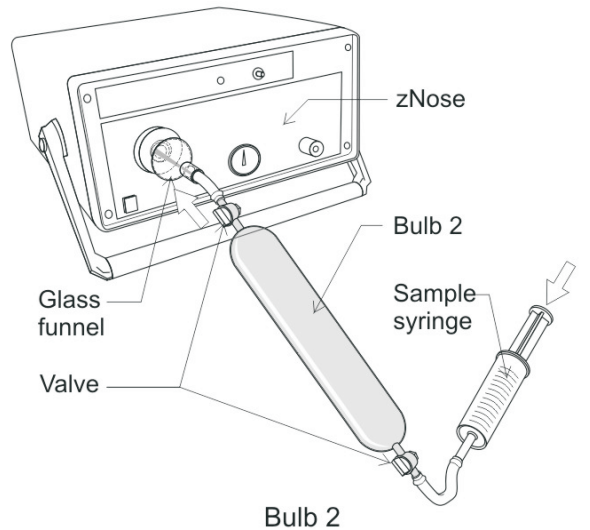
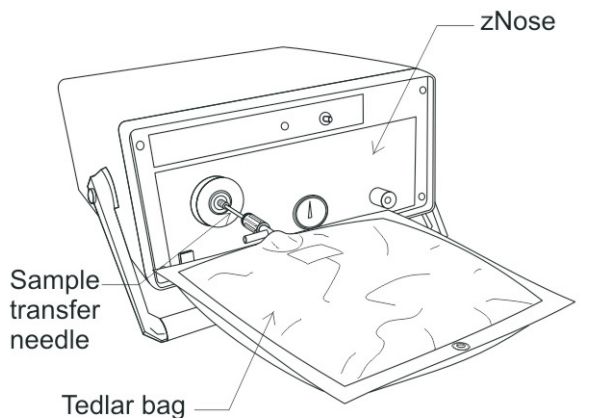


FIG 3 - Sampling from a glass gas bulb.



Tedlar bag - direct

FIG 4 - Sampling from Tedlar bags.

gas-sampling bulb with an aluminium foil septa (Figure 5). The commercially available rubber and foil/rubber composite septa were found to contribute an unacceptably high background to the coal gas samples.

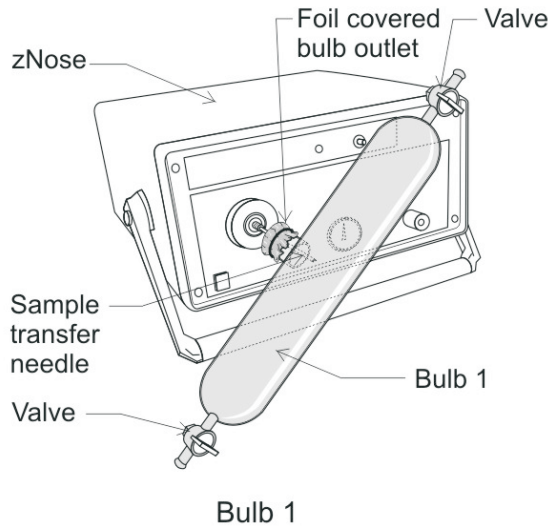


FIG 5 - Analysing gas samples collected from the large-scale test.

Additional gas samples were collected from ports 4 and 5 nearest the heating site and the exhaust port of the 16 m<sup>3</sup> spontaneous combustion reactor (Figure 6) over the temperature range 78.5°C to 123.5°C in order to determine some of the volatile organic and carbonyl species present in the off-gases. The gas samples used for analysis of the volatile organic components were collected by drawing a sample across a Tenax TA ATD tube (automated thermal desorption tube) at 169 ml/min using an SKC Air Chek 224-XR series pump. Gas samples for analysis of the carbonyl components were collected by drawing a sample cross a Supelco DNPH cartridge at 1070 ml/min using a second SKC Air Chek 224-XR series pump.

The volatile organic species were analysed by gas chromatography-mass spectrometry (GC-MS) of the thermally desorbed volatile components from ATD tubes according to Method number 13029 (Christensen, 2003). Carbonyl components

were analysed by solvent elution (3 ml) of DNPH cartridges, followed by high performance liquid chromatography (HPLC) analysis, based on US EPA Method TO11A (Christensen, 2003).

**RESULTS AND DISCUSSION**

**Screening tests**

Four litre aluminised bags are currently used in the mining industry to collect gas samples for permanent gas analysis (H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>) by gas chromatograph. The aluminised bags exhibited a complex background fingerprint. The polymer used to line the aluminised bags and to manufacture the snap in component on which the sampling tube was mounted appeared to be the origin of this fingerprint. The sampling tube itself appeared to have almost no fingerprint (Table 1). The P5.80 peak in the sampling tube spectrum was probably due to residual contamination of the column by the odour component of the polymer lining.

Gas samples drawn from the coal sample, NSW-M1, as it was being reacted in the UQ two-metre column were analysed using the method 18ps-2.mth. In addition to the peaks known to be associated with the polymer components of aluminised bag, peaks at retention times of 1.66, 2.10, 2.42 and 2.95 seconds were identified in the NSW-M1 spectrum (Table 1).

The fingerprint obtained using the glass gas bulbs was less complex than that obtained using the aluminised bags (see Table 2). Peaks previously observed between a retention time of 3.66 to 4.62 seconds were absent indicating these peaks were part of the polymer fingerprint from the aluminised bags and not a background due to laboratory environment. The polymer related peaks P5.80 and P5.98 were reduced by at least a factor of 20. The component appearing at the P2.95 peak in the aluminised bag series was no longer present however the presence of a strong peak at the slightly longer retention time of 3.14 seconds could have been the same component. The retention times of the P1.66, P2.10, P2.42 components were not affected by changing the sampling vessel, indicating a probable coal origin. Some contamination due to a carryover of one of the Tedlar bag fingerprint components was also noted at the P2.84 peak. In addition, four new peaks at retention times of 1.85, 2.60, 4.82 and 5.06 seconds were identified in the glass bulb sampling system.

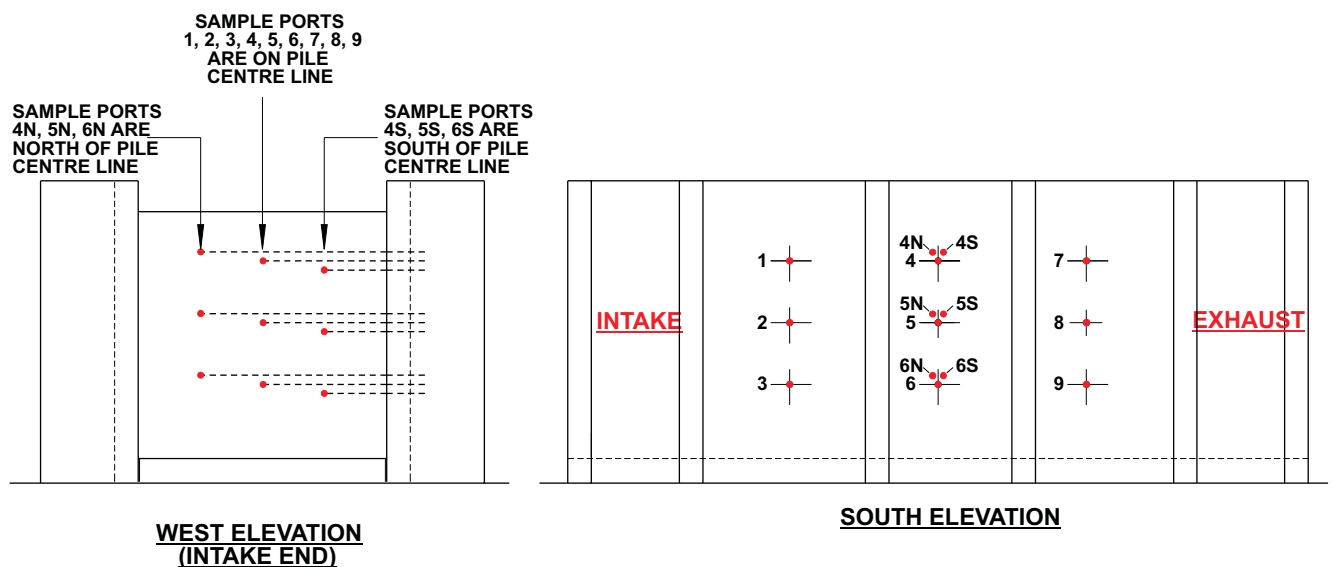


FIG 6 - Coal pile sample tube location and identification.

**TABLE 1**

Components identified in the aluminised gas sampling bags, method 18ps-2.mth.

Peak table (18°C ramp)	RT (sec)	Unused aluminised bag + instrument air	Plastic moulding only	Sampling tube only	NSW-M1 maximum temp 81°C
Counts	Counts	Counts	Counts	Counts	Counts
P1.66	1.66				233
P1.85	1.85		13	13	
P2.10	2.10				21
P2.27	2.27				
P2.42	2.42				136
P2.60	2.60	65	9	23	
P2.84 Tedlar bag	2.84	8			
P2.95	2.95				174
P3.14	3.14	91			
	3.96	128	20		107
	4.20	94	117	41	96
	4.62				53
	4.82	36	59		
	5.06		64		
	5.32	635	161	30	107
P5.80 Aluminised bag	5.76	423	peak	93	1338
P5.98 Aluminised bag	5.98	2096	8268		
	6.78				
P8.12 Rotor peak	8.12	1134	319		91

RT = retention time.

In the Tedlar bag system, the P1.66, P2.42, P4.82 and P5.06 peaks appeared at similar temperatures to those identified in the glass tube system. The P2.60 and P3.14, which occurred either side of the Tedlar bag peak were not detected consistently and in the instances where they could be detected, the temperature tended to be higher. Inspection of the chromatograms indicated that this was because at a column ramp rate of 18°C per second, the adjacent component peaks were not discretely separated from the Tedlar P2.84 peak when present at low levels and therefore could not be detected by the peak detection software (Figure 7). The peak from the Tedlar bag component was of the order of hundreds of counts compared to the adjacent peaks, which were in the order of tens of counts.

Further the P1.85 peak was not detected in any of the coal gas samples and the P2.10 peak was detected over a wider temperature range than in the glass tube system.

Electronic Sensor Technology, the makers of the zNose instrument have reported that the zNose was able to detect both dimethyl acetamide and phenol as the primary contaminants in

**TABLE 2**

Heating fingerprint for NSW-M1 (Newcastle region), method 18ps-2.mth.

Peak table (18°C ramp)	RT (sec)	Glass gas sampling bulbs	Tedlar bags
		Appearance temperature (°C)	Appearance temperature (°C)
P1.66	1.66	20	20
P1.85	1.85	80	ND
P2.10	2.10	80	20
P2.42	2.42	20	20
P2.60	2.60	100	150
P3.14	3.14	60	80
	4.82	20	20
	5.06	20	20

ND = not detected.

RT = retention time.

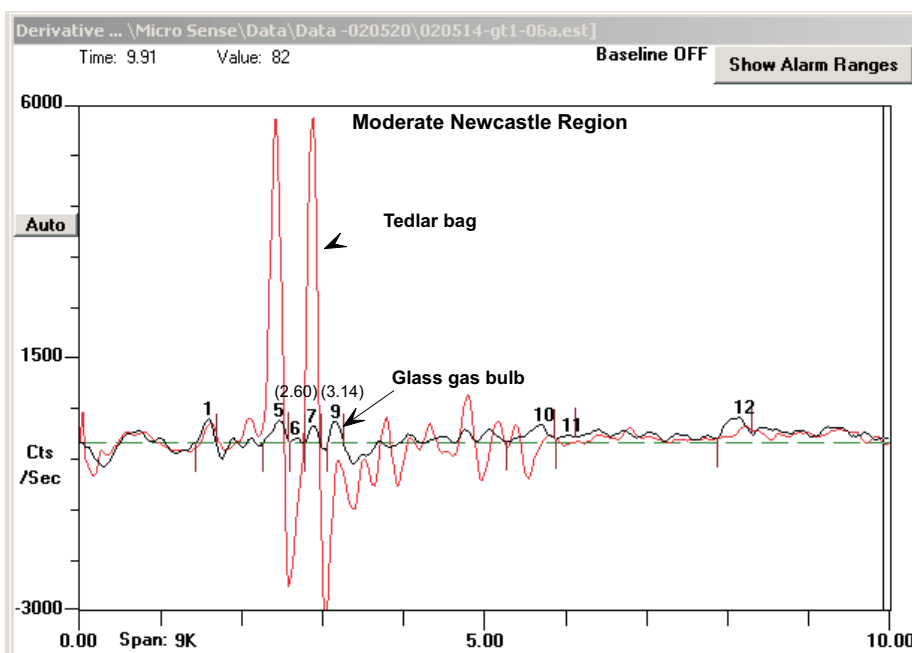


FIG 7 - NSW-M1 gas sample collected at 66°C.

Tedlar bags (Electronic Sensor Technology, nd). They further reported that even after flushing the bags ten times with clean nitrogen, the Tedlar bags continued to outgas these two contaminants at parts per million levels.

**Coal testing – 16 m<sup>3</sup> large-scale spontaneous combustion reactor**

Following optimisation and calibration of the zNose 7100 instrument, a fingerprint peak file R05-s20p20.pkd comprising 21 components was constructed based on the fingerprint for a coal sample heated at 350°C (Table 3). The per cent spread (PCT spread) defines the retention time window within which the zNose will identify a peak as a particular substance.

Analysis of the port 4 and 5 gas samples using the method R05-s20p20.mth found that no components (ie volatile organic compounds (VOCs)) corresponding to the fingerprint defined in the R05-s20p20 peak file were reliably detected below 87°C. The P8-DW and the singlet-doublet peak component (4.04) were the first fingerprint components detected and had a temperature range of 87°C to 189°C and 87°C to plus 400°C respectively (Figures 8 - 10). Two other fingerprint components were detected at 92°C, namely the P6-DW peak and the P10-DW peak. The concentration of these components together with that of the P8-DW component appeared to increase with temperature (Figure 11) indicating these components were either products of the oxidation of coal or were volatile organic compounds tightly bound to the coal surface which desorbed as the coal self-heats.

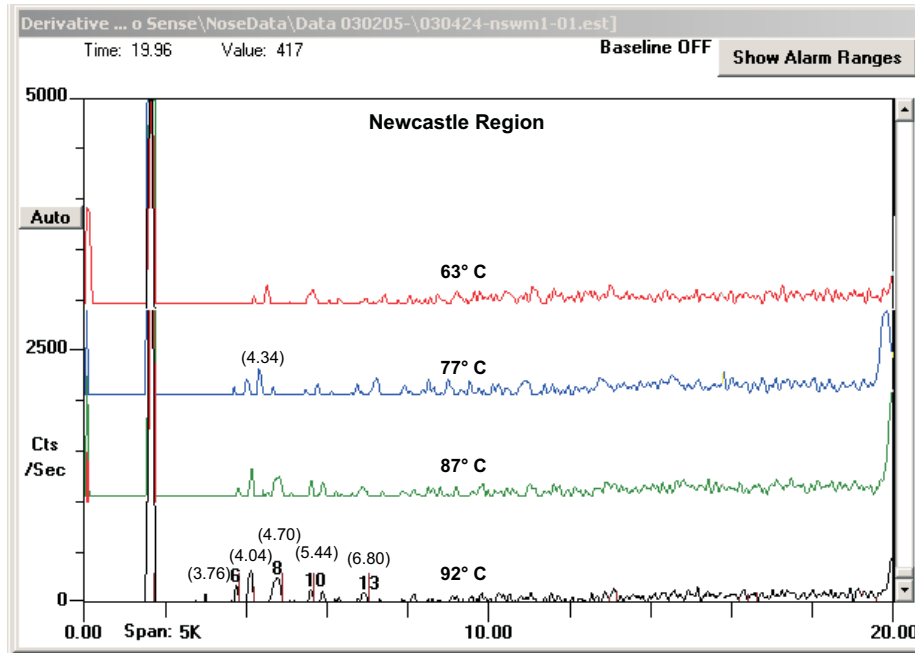


FIG 8 - Low temperature VOC fingerprint profile of NSW-M1.

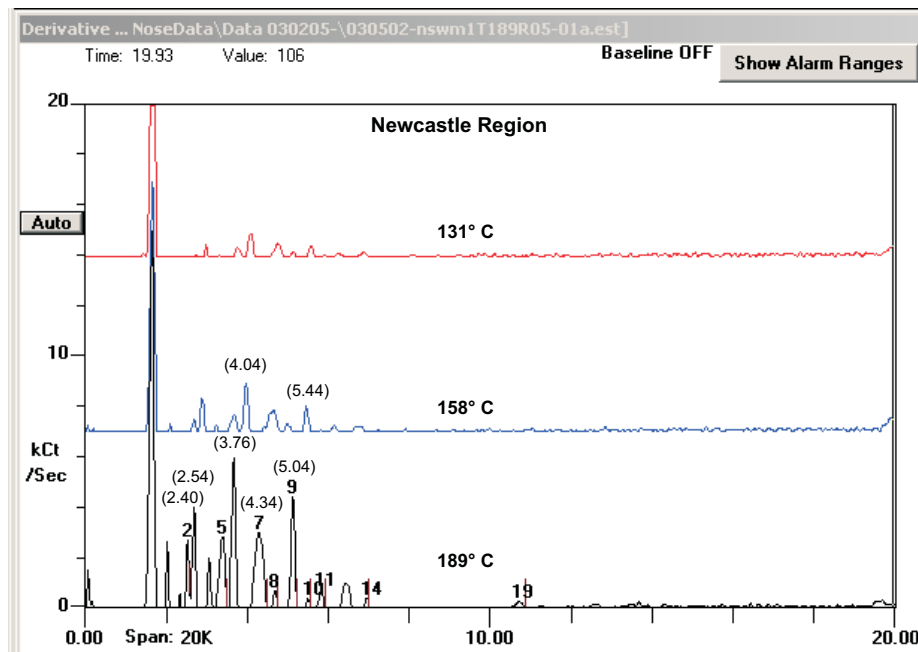


FIG 9 - Advanced heating VOC fingerprint profile of NSW-M1.

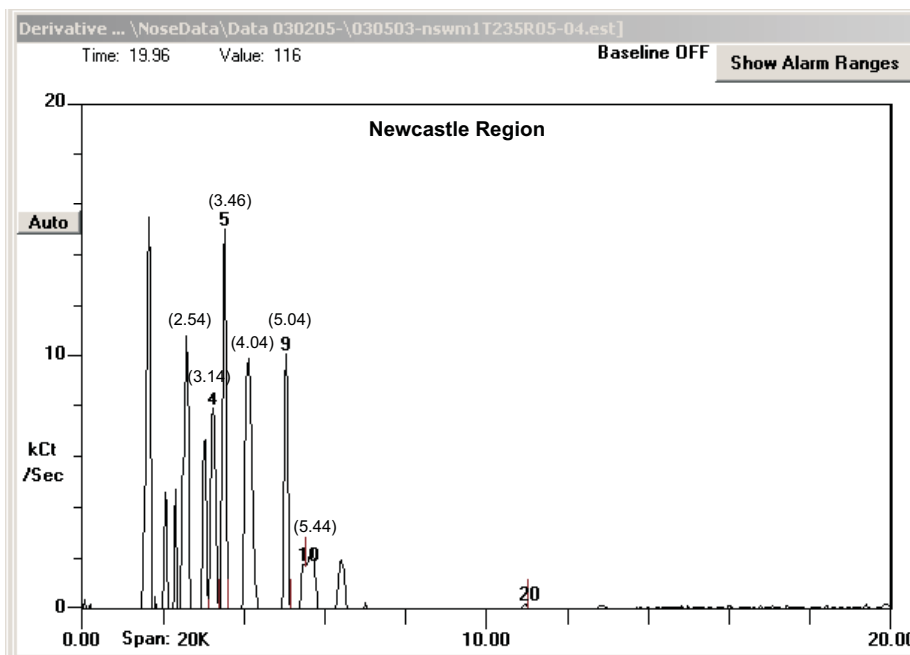


FIG 10 - VOC fingerprint profile of NSW-M1 at 235°C.

**TABLE 3**

Parameters for peak file, R05-s20p20.pkd.

Substance	RT (sec)	PCT spread
P1-DW, 2.16	2.16	2.5
P2-Toluene, 2.4	2.40	4.0
P3-DW, 2.74	2.74	2.5
P4-DW, 3.14	3.14	2.5
P5-DW, 3.46	3.46	3.5
P6-DW, 3.76	3.76	2.5
P7-DW, 4.34	4.34	2.5
P8-DW, 4.70	4.70	2.5
P9-DW, 5.04	5.04	2.5
P10-DW, 5.44	5.44	2.5
P11-DW, 5.84	5.84	2.3
P12-DW, 6.12	6.12	2.3
P13-DW, 6.80	6.80	1.5
P14-DW, 7.02	7.02	1.5
P15-DW, 7.9	7.90	2.5
P16-DW, 8.60	8.60	2.5
P17-DW, 9.10	9.10	2.5
P18-DW, 9.72	9.72	2.5
P19-DW, 10.41	10.41	2.5
P20-DW, 11.06	11.06	2.5
P21-DW, 11.64	11.64	2.2

PCT spread = per cent spread

RT = retention time.

At higher temperatures, a number of other VOC components were detected with retention times of less than 3.76 seconds (P6-DW component) (Figure 9). Given that the instrument separates and therefore detects VOC compounds on the basis of their volatility, ie the smaller the retention time the more volatile

**TABLE 4**

Heating fingerprint of NSW-M1 sample – ports 4 and 5 components.

Peak Table (5°C ramp)	RT (sec)	Coal temp (°C)
	2.02	189
P1-DW	2.16	ND
	2.26	235
P2-Toluene	2.40	189
	2.54	158
P3-DW	2.74	ND
	2.98	131
P4-DW	3.14	158
P5-DW	3.46	189
P6-DW	3.76	92
singlet - doublet	4.04	92
P7-DW	4.34	189
P8-DW	4.70	87
P9-DW	5.04	131
P10-DW	5.44	92
	5.60	235

ND = not detected

RT = retention time.

the compound, it can be inferred that these components were smaller more volatile organic species than those occurring at the P6-DW, singlet-doublet (4.04), P8-DW, and P10-DW retention times. It was also possible that these more volatile compounds were products of incomplete oxidation of the coal.

The VOC components with retention times of greater than 5.60 did not appear to be related to the low temperature heating of the NSW-M1 coal as the detected concentrations did not change or trend significantly with temperature. The appearance temperatures of the VOC components analysed using the method R05-s20p20.mth are summarised in Table 4.

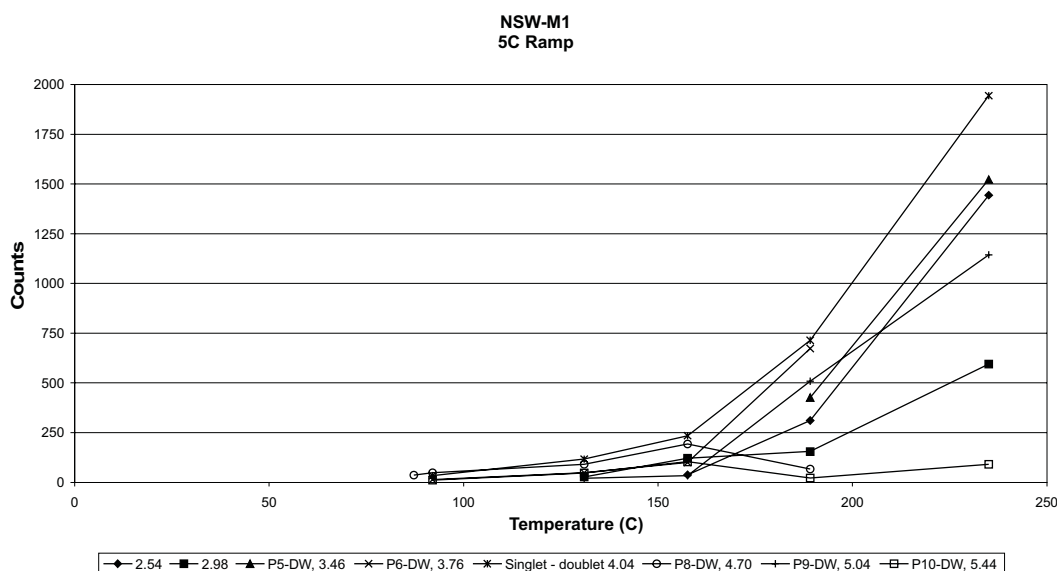


FIG 11 - Dependence of NSW-M1 VOC components on coal temperature.

### Gas chromatography – mass spectrometry and high performance liquid chromatography analysis

The gas chromatography-mass spectrometry (GC-MS) analysis of the off gases from the 16 m<sup>3</sup> spontaneous combustion reactor indicated the presence of C6 - C9 alkanes, several ketones and aromatic benzene compounds below 100°C (Table 5). The alkane and ketone compounds appeared to increase in concentration with increasing temperature below 100°C although there was some uncertainty as to the size of the increase for the hexane and heptane samples due to the high sample concentration on the ATD tubes. With the exception of benzene, the aromatic benzene type compounds did not appear to increase with temperature below 100°C. The higher concentrations of the alkane, ketones and aromatic benzene compounds measured in the exhaust port gases compared to ports 4 and 5 indicate that these compounds were being produced over a wider area than just the port 4 and 5 locality and that their participation in absorption or secondary reactions within the coal pile was limited. Therefore, these compounds were stable enough to be expected to be released into the goaf air. The stability of these compounds once in the goaf type environment was not determined.

The high performance liquid chromatography (HPLC) analysis of the off gases from the 16 m<sup>3</sup> spontaneous combustion reactor indicated the presence of a number of carbonyl components (oxygenated species) in the off-gases (Table 6). The presence of formaldehyde appeared to be temperature dependent, increasing in concentration between 75.8°C and 123.5°C. The temperature dependence of the evolution of acetaldehyde, acetone, propionaldehyde and the heavier more complex oxygenated species was not clear from the current data.

The lower concentrations of acetaldehyde, acetone and propionaldehyde in the exhaust port gases indicated these oxygenated species were probably being absorbed within the coal pile to some degree. The potential for these gases to be found in the goaf was therefore limited. However if they were detected in goaf gas samples, this could indicate that the site of the heating was close to the sampling point. The higher levels of formaldehyde in the exhaust port were most likely due to the fact that it is a small highly volatile compound and, therefore, did not readily absorb onto the coal as it traversed the coal pile.

Overall the aromatic hydrocarbons and, to a limited degree the oxygenated forms of the volatile organic compounds, appeared to coexist rather than one in preference to the other.

**TABLE 5**GC-MS results for 16 m<sup>3</sup> spontaneous combustion reactor.

Reactor max temp (°C)	75.8	86.3	86.3
Port	4 and 5	4 and 5	Exhaust
Compound name	Amount (µg/L)	Amount (µg/L)	Amount (µg/L)
Dichloromethane	<RL	<RL	<RL
Methyl ethyl ketone	0.079	0.282	0.449
Ethyl Acetate	<RL	<RL	<RL
n-Hexane	0.197 <sup>†</sup>	0.807 <sup>†</sup>	1.061 <sup>†</sup>
Chloroform	<RL	<RL	<RL
1,1,1-Trichloroethane	<RL	<RL	<RL
Benzene	0.014	0.039	0.057
Trichloroethene	<RL	<RL	<RL
n-Heptane	0.500 <sup>‡</sup>	0.780 <sup>‡</sup>	1.489 <sup>‡</sup>
Methyl isobutyl ketone	0.010	0.015	0.024
Methyl cyclohexane	0.309	0.578	0.796
1,1,2-Trichloroethane	0.001	0.003	0.003
Toluene	0.016	<RL	0.020
n-Octane	0.184	0.309	0.551
Tetrachloroethylene	0.001	<RL	<RL
1,1,1,2-Tetrachloroethane	<RL	<RL	<RL
Ethyl benzene	0.012	0.002	0.017
m- and p-Xylene	0.004	0.005	0.010
1,1,2,2-Tetrachloroethane	<RL	<RL	<RL
2-Butoxyethanol	0.001	<RL	0.003
o-Xylene	0.003	0.003	0.007
n-Nonane	0.064	0.112	0.188
1,3,5-Trimethylbenzene	0.002	0.002	0.004
1,2,4-Trimethylbenzene	0.002	0.003	0.005
n-Decane	<RL	<RL	<RL
1,2,3-Trimethylbenzene	0.001	0.001	0.002

&lt;RL Less than reporting limit of 10 ng on tube.

† Results indicated with † were above the calibration range.

‡ Results for the port 4 and 5 123.5°C sample were not available, because the computer crashed during acquisition.



TABLE 6

Carbonyl components results for 16 m<sup>3</sup> spontaneous combustion reactor.

Reactor max temp (°C)	75.8	86.3	123.5	86.3
Port	4 and 5	4 and 5	4 and 5	Exhaust
Compound name	Amount (µg/L)	Amount (µg/L)	Amount (µg/L)	Amount (µg/L)
Formaldehyde	0.0171	0.0317	0.1246	0.0419
Acetaldehyde	1.2305	1.1814	1.4294	0.4189
Acrolein	<RL	<RL	<RL	<RL
Acetone	0.0327	0.0670	0.0367	0.0161
Propionaldehyde	0.0405	0.0300	0.0568	0.0097
Crotonaldehyde	<RL	<RL	<RL	<RL
2-Butanone	<RL	<RL	<RL	<RL
Methacrolein	0.0047	0.0053	0.0073	<RL
Butyraldehyde	0.0171	0.0123	0.0312	<RL
Benzaldehyde	<RL	<RL	0.0073	<RL
Valeraldehyde	0.0125	0.0053	0.0312	<RL
p-Tolualdehyde	<RL	<RL	<RL	<RL
Hexaldehyde	0.0047	<RL	0.0128	<RL

<RL Less than reporting limit of 0.15 µg on tube

### Implications for applying electronic nose technology to detection of heating of coal at low temperatures

While it was possible to define a fingerprint that could be used to characterise the heating profile of a coal sample, the main discrimination achievable was that *an advanced heating did or did not exist*.

It is clear from the zNose results that the levels of VOCs produced by a low temperature heating (ie less than 100°C) are very small compared to other sources of VOCs present in gas sampling media. This includes media such as the aluminised bags and Tedlar bags which are routinely used to handle coal gas samples. In order to obtain a reasonable baseline to enable detection of the VOC components of the coal gas spectrum, it is necessary to go to inordinate lengths to identify and remove items from the sample handling and collecting system which have a characteristic VOC profile of their own. This is important as the higher levels of background VOCs either overlap the coal VOC spectrum or overload the instrument column and/or sensor before a useful loading of coal VOC components can be achieved. Maintaining a 'clean' sampling system in the mine situation is much more difficult than in a controlled laboratory environment.

Further as a result of the contamination issues, gas samples could only be collected in glass gas bulbs and vials which had to be sealed with an aluminium foil septa. The commercially available rubber and foil/rubber composite septa were found to contribute an unacceptably high background to the coal gas samples. A suitable substitute for the aluminium foil septa was not identified during the project. This would need to be done if further work was undertaken as the use of aluminium is restricted in underground coal mines.

The low levels of VOCs present in the coal signature below 100°C would also represent a significant challenge in detecting a low temperature heating in the mining environment as, in all likelihood, VOC emissions from diesels, plastics and electrical equipment used in the mine could produce a significant background of their own and swamp the coal VOC signature. Even the electronic noses using metal oxide, conducting polymer

and quartz microbalance sensors which respond to a wider range of compounds could be compromised by the 'uncontrolled' mine environment. Potentially they could return either a false positive or exhibit so little change on a contaminant loaded sensor that no measurable change might register until the heating was at an advanced stage. It is not possible to assess the potential sources of contamination or their ability to bias sensor readings without knowing more about the nature of the low temperature coal emissions, the mining environment and the sensor's affinity for specific compounds.

The major implication from all these factors is that a better understanding of the range of volatile compounds that are or are not present from low temperature coal heating is required together with a knowledge of the compounds routinely found in the mine atmosphere. This is necessary in order to determine if electronic noses or even other analytical techniques can be applied to the detection of a low temperature heating.

In particular there is a need to determine the presence or otherwise of:

1. oxygenated species such as acetone, methanol, formaldehyde,
2. volatile organic compounds such as benzene, toluene, hydrocarbons, and
3. sulfur compounds.

This knowledge will then allow an assessment to be made as to whether, besides the currently used CO and CO<sub>2</sub> profiles, there exist any gases below 100°C that have the potential to be used as an indicator of a low temperature heating. The limited GC-MS and HPLC work undertaken as part of this project has confirmed that some oxygenated and VOCs do exist in coal heated at less than 100°C however there is insufficient data available to determine if they have a potential to be used as heating indicators.

## CONCLUSIONS

Very low levels of volatile organic compounds are emitted from coal below 100°C. Alkanes C<sub>6</sub> - C<sub>9</sub>, several ketones, aromatic benzene compounds, acetone, formaldehyde and several other oxygenated compounds are present in gas samples from coal reacting below 100°C. The low temperature range over which these volatiles are emitted from coal is not well described.

The zNose instrument has shown some capacity to detect a heating below 100°C but this ability was easily compromised by contaminants in the sampling system. Aluminised gas sample bags and Tedlar bags give off significant levels of volatile organic compounds, which contaminated the coal gas samples. Use of glass gas sample bulbs and vials sealed with aluminium foil was necessary to avoid contamination of the coal gas samples. The zNose was able to discriminate as to whether a heating is at an advanced stage or not. Hence, the zNose instrument was capable of providing detailed fingerprints of gases evolved during coal heating once an advanced (ie pyrolysis) stage is reached.

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.

## ACKNOWLEDGEMENTS

The contributions of Simtars staff past and present to this project is gratefully acknowledged. The permission of the director of Simtars, Stewart Bell to publish this paper is also gratefully acknowledged. This work was supported by ACARP and Centennial Coal Company Limited.

## REFERENCES

- Christensen, E, 2003. Report No 02PW 1034/42, Queensland Health Scientific Services.
- Clarkson, F, 2004. Detection of heating of coal at low temperatures, Interim report, Australian Coal Association Research Program project number C10015 Report (ACARP: Brisbane Australia).
- Cliff, D, Rowlands, D and Sleeman, J, 1996. *Spontaneous Combustion in Australian Underground Coal Mines* (ed: C Bofinger), (Simtars: Redbank Australia).
- Electronic Sensor Technology, nd. The problem with Tedlar bags [online]. Available from: <<http://www.estcal.com>>, p 1-6.
- Hester, C and Clarkson, F, 2003. Z Nose Project progress report – March 2003, Simtars report OG172229P3 (Simtars: Redbank Australia).
- Higuchi, K and Ohga, K, 1997. Early detection system of mine fire using smell sensors, in *Proceedings 27th International Conference of Safety in Mines Research Institutes* (eds: B B Dhar and B C Bhowmick) vol 2, pp 925-934 (Oxford and IBH Publishing Co Pvt Ltd: New Delhi).
- Ohga, K and Higuchi, K, 1995. Early detection of mine fire in underground by using smell detectors, in *Proceedings Seventh US Mine Ventilation Symposium*, pp 231-236 (Society for Mining, Metallurgy and Exploration Inc: Littleton).
- Ohga, K, Zhenyu, W, Qingyang, W and Mitsumasu, M, 1999. Japan/China research cooperation on prevention of spontaneous combustion – fundamental study on change of smell generated by spontaneous combustion of coal, *Coal and Safety*, 14:48-52.
- Zubritsky, E, 2000. E-Noses keep an eye on the future, *Analytical Chemistry*, 72(11):421A-426A.