The Measurement of Decomposition Products Of Select Gases As an Indicator of a Concealed Mine Fire

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ABSTRACT

Currently, techniques used to determine whether or not there is a concealed fire in an inaccessible area of a coal mine are not definitive. Inaccessible areas of coal mines include:

1. A mined-out area, such as a longwall gob.
2. A mine area, or entire mine, that has been sealed to extinguish a fire.
3. The interior of pillars in a mine.
4. Abandoned mines.

Mined-out areas – gobs – are particularly problematic. The standard practice is to obtain measurements for gas concentrations from an inaccessible area, and to apply certain rules to the obtained concentrations in order to decipher whether or not there is a fire in the area. Unfortunately, none of the gas measurements, and the associated rules that are applied, are free of potential problems. Therefore, there is always some degree of uncertainty in any decision that is based on the current methods.

A more definitive method of determining whether or not a concealed fire exists would be valuable; perhaps avoiding unnecessary exposure of miners to risks, and unnecessary exposure of mining companies to economic loss. This study details the inadequacies of the current methods for determining the presence of a fire in an inaccessible area of a coal mine, and proposes two novel methods for overcoming the current inadequacies.

The first method that was proposed, and studied, involves looking for the presence of the radioisotope carbon-fourteen in the carbon monoxide in the return airways of coal mines. For the vast majority of coal mines, if there is no fire anywhere in the coal mine, carbon monoxide should not have any carbon-fourteen in it. If there is a fire, the carbon monoxide should have carbon-fourteen in it. This method is based on the Boudouard Reaction, which documents a reaction between carbon, carbon monoxide, and carbon dioxide that occurs at temperatures that only occur with a fire. Because of the very small amounts of carbon-fourteen in carbon dioxide in the atmosphere, and the small amount of carbon monoxide usually present in a coal mine atmosphere, there does not appear to be any way, currently, to implement this method. Instrumentation that may allow implementation of this method, in the future, is discussed.

The second method, that was proposed and studied, involves introducing a select, gaseous, organic compound into an inaccessible area; and then using a gas chromatograph to test for the presence of definitive fire decomposition products of the initial organic compound in the atmosphere that is exiting the inaccessible area.

Laboratory tests, conducted as part of the study of the second method, established the concept of this novel method of using select, organic compounds for definitively determining whether or not a concealed fire exists in an inaccessible part of a coal mine. Based on an initial screening of 5 different compounds, two compounds have been selected for use as fire indicator gases (FIGs). These two compounds are:

1. C6-Perfluoroketone ($CF_3CF_2C(=O)CF(CF_3)_2$)
2. 1,1 Difluoroethane (CH_3CHF_2)

This study provides suggestions as to how to look for other potential FIGs, and how to improve the testing of potential FIGs.

Examples of all four of the types of inaccessible areas listed above are discussed, particularly from the viewpoint of how FIGs could be utilized in each case, and how FIGs could provide better information in each case.

In addition, as a by-product of the experiments conducted for this work, this study identifies at least six gases that might be used simultaneously as tracer gases for complex ventilation studies in a mine, or elsewhere.

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Chapter 1: Introduction

For more than a century, researchers have been trying to develop better methods of ascertaining whether or not there is a fire in a coal mine. Of course, considerable progress has been made with respect to open, accessible parts of a coal mine. For example, beltways are now routinely monitored with sensitive carbon monoxide sensors that relay measurements to a central monitoring station. However, problems still exist for inaccessible areas, such as mined out areas, where a fire can be concealed. Most methods of monitoring for fire are not available for an inaccessible area. Usually, monitoring of gases that are exiting the area is the only available method. Sometimes, gas readings can give ambiguous results. Serious questions usually arise when there is the potential for spontaneous combustion to initiate in a gob, or an ignition has occurred in a gob; or when an area of a mine has already been sealed because of a fire, and information is needed as to whether or not it is safe to reopen the sealed area.

Chamberlain, Hall, and Thirlaway give a brief history of efforts to deal with the spontaneous combustion of coal, and coal fire detection. These authors mention that one of the earliest papers that investigated spontaneous combustion, in coal stockpiles, was written by a Professor Plot of Oxford, in 1686. They also note that several papers that were published during the period 1848 – 1870 noted some of the changes in coal that occurred when coal was exposed to air, and suggested that absorption of oxygen was an important factor. By the end of the 1800's, the ability of coal to react with oxygen at ambient temperatures, and produce carbon monoxide, had been established by laboratory tests. An increasing amount of research into the oxidation of coal during the period of 1900 to 1940 culminated in the work of Graham and others that yielded a method for the detection of spontaneous combustion, based on the production of carbon monoxide (CO) and the consumption of oxygen, that is still used today. (Chamberlain, Hall, and Thirlaway, 1970, pp.1-2).

Therefore, for inaccessible areas, such as mined out areas, techniques that originated almost a century ago are still relied on. Graham's development, in 1920, of the CO – Oxygen Deficiency ratio is still the primary basis for judging whether or not a fire has developed in inaccessible areas, or whether a sealed fire is finally smothered. (Graham, 1921). Other gas readings and ratios have been proposed through the years, but all these proposed methods, including Graham's, have potentially serious problems and limitations, as will be described below. Sudhish Banerjee, in his recent book titled, *Prevention and Combating Mine Fires*, notes that there is still considerable effort aimed at developing better coal mine fire detection methods. (Banerjee, 2000, p. 147)

Currently, a coal mine is sometimes shut-down and sealed because of a concern that there is potentially a concealed fire in an inaccessible part of the mine. This concern is usually generated by an observation that the amount of CO in the air that is exiting a mine, or a return from a gob area, has risen slightly above an ambient level. Such observations are not always definitive, potentially exposing workers to unnecessary risk, or mine operators and workers to unnecessary economic loss. The rise in the amount of CO might not be so great as to clearly indicate a fire, and might not be so small as to obviously be within what might be expected to be simple, normal fluctuations. This condition is typically brought about because of the possible dilution of fire gases by the ventilating air streams. An incipient fire in a small area of a gob can produce CO, and other fire gases, in a concentrated amount, but by the time these fire gases reach a point where they can be measured, these gases can be considerably diluted. Mitchell notes that by the time miners become aware of the possibility of spontaneous combustion in a gob area by observing higher than normal levels of carbon monoxide, the chances are that the oxidation reaction has gone beyond easy control. (Mitchell, 1996, p.29) He also lists considerable cautions concerning using gas measurements to determine if it is safe to reopen a sealed area after a fire. (Mitchell, 1996, pp.125-133) These, and other cautions that will be elaborated on below, emphasize that current methods of determining whether or not there is a concealed fire in an inaccessible part of a coal mine suffer from significant problems. A complete overview of the different mine gas ratios and indices that have been developed, and used, over the last century are reviewed in Chapter 2. All the different problems and disadvantages with all these ratios and indices are detailed.

Some method is needed that would give a more definitive indication of a concealed fire than the current methods do. Two possible, novel methods were examined during this study. The first method involves the distribution of radiocarbon – ^{14}C – between carbon monoxide (CO) and carbon dioxide (CO_2) in a mine atmosphere. The argument is presented that, under non-fire conditions, the CO in a mine atmosphere should not have any ^{14}C in it. However, during fire conditions – due to the Boudouard Reaction – the CO in a mine atmosphere will have ^{14}C in it. Details of the reaction, and possible methods for checking for the presence of ^{14}C in CO, are presented in Chapter 3.

The second method for testing for the presence of fire in an inaccessible area of a coal mine involves the examination of different chemical compounds that would be gases at typical mine temperatures; and that, when introduced into an inaccessible area, might yield novel decomposition products when exposed to the elevated temperatures that would only be associated with a fire. Likely candidates for such a fire indicator gas are various halogenated organic compounds that would not have any deleterious attributes, such as toxicity; and would potentially yield unique decomposition products that also have no deleterious attributes. A method for screening for likely fire indicator gases is explained in Chapter 4. Several such compounds were examined as part of this study. Experiments were performed on five possible fire indicator gases, and two of these initial compounds yielded distinctive breakdown products. Details of these tests are provided in Chapter 5.

In Chapter 6 of this paper, some real-life examples of mine fires are examined; with a discussion of how fire indicator gases might help clarify situations that are uncertain, when examined with gas ratios and indices. The real-life examples include:

1. A spontaneous combustion, or ignition, in a mined-out area, such as a long-wall gob.
2. A mine area, or entire mine, that has been sealed to extinguish a fire.
3. Fires that develop in coal pillars in a mine.
4. Fires that occur in abandoned mines.

Typical questions that arise, in coal mine fire situations, that fire indicator gases might answer more definitively than currently used gas ratios and indices, include:

1. Is there a fire?
2. Where is the fire located?
3. What is the extent of the fire?
4. Are efforts to fight or contain the fire meeting with success?
5. When is it safe to reopen the mine?

How fire indicator gases could be used to answer these questions for a concealed fire is addressed in Chapter 6, with examples of historic fires.

Chapter 2: Literature Review

A literature review was conducted in order to establish the current state of knowledge concerning:

1. Recent underground coal mine fire history.
2. Spontaneous combustion of coal.
3. Methods currently used to detect concealed, underground coal mine fires.
4. Novel gases that might be used to better detect such fires.

2.1 Recent Underground Coal Mine Fire History

During the time period from 1990 through 2007, there were a total of 138 fires in underground coal mines in the United States that were reportable in accordance with regulations of the United States Mine Safety and Health Administration. (Trevits, Yuan, Smith, Thimons, 2008, p. 358)

Mine fires can be grouped into either "open" fires – fires that occur in open, active parts of a mine; or "concealed" fires – fires that occur in abandoned or otherwise inaccessible areas, such as gobs. There are more, and better, choices for the detection and fighting of open fires. Of course, concealed fires represent a larger problem because of limited accessibility, which limits detection and firefighting choices. The detection methods available for both open and concealed mine fires will be discussed below.

It is noteworthy that, of the 138 fires from 1990 through 2007, 25 were due to spontaneous combustion, which often occur in inaccessible gob areas, and therefore may not be readily detected. (Yuan and Smith, 2008) Three of the 25 spontaneous combustion fires resulted in methane gas explosions.   The incidence of such fires, and the associated risk of explosions, is expected to increase with the mining of lower ranked coals, the mining of deeper seams with more methane gas, and the growth in the size of longwall panels. (Trevits et al, 2008, p. 359)

Concern with concealed fires, especially spontaneous combustion, is not limited to coal mining in the United States. Singh, et al. (2007, p. 192) state that coal mine fires are still a serious problem for the Indian coal mining industry, and that most fires occur due to spontaneous combustion. Ham, in a 2005 review of spontaneous combustion incidents in Australia, notes that over the previous five years there had been an increase in the number of spontaneous combustion incidents. He documented 88 spontaneous combustion incidents that had occurred between 1972 and 2004, while conceding that the data was not complete. Three of these incidents resulted in explosions that killed a total of 41 miners. (Ham, 2005, p.238)

There are other situations where a coal mine fire can be concealed, other than in a gob area. Another example of a type of concealed fire is the case of spontaneous combustion of coal within the body of a coal pillar. Timko and Derick, in the 1995 United States Bureau of Mines Report of Investigation Number 9553, describe how a large pressure differential across coal pillars in a stopping line can induce leakage not only through the stoppings but also through the pillars. If the coal is susceptible to spontaneous combustion, the airflow through the natural fractures of the pillar can induce spontaneous combustion. These authors conducted tests that allowed them to locate a “heating” in a pillar, but concluded that: “...the ability to accurately predict future spontaneous heating events remains in question.” (Timko & Derrick, 1995, p. 1)

Yet another example of a type of concealed fire, but in this case involving surface areas, is that of stockpiles and waste piles.

A related problem to simply detecting concealed coal mine fires is the problem of determining when it is safe to re-open an area of a mine that was sealed in order to attempt to suffocate a fire. As Mitchell points out, this problem is especially tricky because a sealed coal fire can still retain a considerable amount of heat, and smolder for long periods of time after oxygen levels in the sealed area have fallen to near zero. (Mitchell, 1996, p. 121) Reopening the sealed area too soon will result in the fire rekindling, resulting in further delays before a mine can be put back into production. Waiting beyond the time necessary for the fire to be truly extinguished also results in an unnecessary delay and loss of production.

No matter what the exact nature of a concealed coal fire is, two factors are almost always present. Spontaneous combustion is a leading cause, and gas measurements play a large role in detection and monitoring.

2.2 Spontaneous Combustion of Coal

As noted in the introduction, published accounts of problems due to spontaneous combustion of coal date back several centuries. Speight (2013) summarizes several points about the spontaneous combustion of coal. Spontaneous combustion of coal can occur because different ranks of coal can undergo an oxidation reaction at ambient temperatures. Under favorable circumstances, the oxidation reaction can occur at a progressively rapid rate – known as “thermal run-away” – resulting in a rapid enough oxidation reaction to be called a fire. The amount of air flow into and through a mass of coal is critical. There must be a large enough flow of air – with its oxygen content – through a mass of coal to allow a large enough oxidation reaction of a volume of coal to take place to generate enough heat to constitute a fire. If a mass of coal is not permeable enough to air flow, a progressively rapid oxidation reaction will not occur. On the other hand, if a mass of coal is too permeable to air flow, an oxidation reaction can still take place, but now the extra air flow will carry off the heat generated by the reaction too quickly, and the mass of coal will not experience the build-up of heat necessary to allow the thermal run-away reaction to progress to a fire stage. (Speight, 2013, p. 367)

Speight lists a number of factors that influence to what degree a coal may be susceptible to spontaneous combustion, including particle size, rank, volatile content, moisture content, oxygen content, and pyrite content. Generally, as the rank of coal decreases, the possibility of spontaneous combustion increases. In general, when a coal is thoroughly dried, the rate of oxidation of the coal decreases. However, if a dry coal is exposed to moisture, heating of the coal may increase. This may be due to some combination of a heat of wetting, along with the formation of oxygen radicals. (Speight, 2013, pp. 265-267)

Smith and Lazzara note that spontaneous combustion of coal continues to represent a significant hazard to life and property. (Smith & Lazzara, 1987, p. 2) They determined the minimum self heating temperatures of 24 coals representing all ranks from lignite to anthracite. The minimum self-heating temperature is the minimum initial temperature that produced a sustained exothermic reaction, or thermal runaway. If a mass of coal were to reach this temperature, perhaps by initial, ambient oxidation, spontaneous combustion is inevitable. Their table of determined minimum self-heating temperature values is reproduced here as Table 1.

Table 1

Minimum Self-Heating Temperatures (SHT) of Various Coal Seams Ordered by Relative Self-Heating Tendency

Apparent Rank: lig = lignite; hvCb = High Volatile C Bituminous; hvAb = High Volatile A Bituminous; lvb = Low Volatile Bituminous; mvb = medium volatile bituminous; an = anthrcite (adapted from Smith & Lazarra, 1987, p. 10, Table 2)

Seam	Apparent Rank	Minimum SHT, °C
Lehigh bed	lig	35
No. 80-1	hvCb	35
No. 80-2	hvCb	40
F	hvCb	45
Beulah-Zap	lig	60
E-1	hvAb	65
E-2	hvAb	65
B-1	hvAb	70
No. 6	hvCb	70
B-2	hvAb	75
Clarion	hvAb	75
D-2	hvAb	80
Lower Sunnyside-2	hvAb	80
Lower Sunnyside-1	hvAb	85
D-1	hvAb	90
Pittsburgh	hvAb	90
Lower Kittanning	hvAb	100
Pocahontas 3-2	lvb	110
Pocahontas 3-1	lvb	115
Coal Basin-1	avb	120
Coal Basin-2	avb	120
Blue Creek	lvb	135
Mary Lee	lab	135
Anthracite	an	>140

As summarized in Table 1, Smith and Lazarra concluded that the relative self-heating tendencies of coals, based on the measured minimum self-heating temperatures, increased with decreasing rank. Lignite and high-volatile bituminous coals had a relatively low self-heating temperature, whereas anthracite had no tendency to self-heat. They also demonstrated that the self-heating tendency of a coal increased when a dry coal was exposed to humid air.

Kuchta et al. add some additional information, noting that the auto-ignition temperature of coal is approximately 150 degrees Celsius, and that the flaming combustion stage for coal fires can reach about 1000 degrees Celsius. (Kuchta, Furno, Dalverny, Sapko, & Litton, 1982, p. 19)

Cliff, in 2005, addressed current issues with spontaneous combustion in Australian coal mining. One of his main contentions was that, with the change in mining methods through the years, classical methods for detecting spontaneous combustion needed to be re-examined. He noted that monitoring for spontaneous combustion has meant monitoring for certain gases, especially carbon monoxide, and determining whether particular gas concentrations, or ratios of gas concentrations, exceeded preset limits. He notes that most spontaneous combustion events now occur in longwall gobs, and that these events indicate that the detection process is "less than perfect." (Cliff, 2005, p. 219)

2.3 Current State of Fire Detection in Coal Mines

Hertzberg, in his article titled "Mine Fire Detection," that appeared in a United States Bureau of Mines Information Circular Number 8768, gave a good summary of methods of mine fire detection. He divided underground mine fires into three types: (Hertzberg, 1978, p. 39)

1. A rapidly developing, open fire.
2. An incipient fire in equipment.
3. A spontaneous combustion fire in the coal seam itself, in a gob area, or in a sealed area.

It might be noted that other authors have somewhat different categorizations of types of coal mine fires. For example, Mitchell simply divides coal mine fires into two categories: “open” and “concealed.” (Mitchell, 1996, p. 27)

Hertzberg then divided the methods of detecting mine fires by five types of detectors:

1. Thermal.
2. Optical.
3. Products of combustion.
4. Flow field, or aerodynamic.
5. Human.

He then provides some details for these different detectors: (Hertzberg, 1978, pp. 40-42)

1. There are several different types of thermal sensors, all of which require that the sensor be very close to the fire.
2. Optical sensors must actually “see” energy emitted by heating, and therefore are limited by field of view constraints.
3. Products of combustion include gases such as carbon monoxide and carbon dioxide, smoke, submicron particles, and products of pyrolysis of coal and other combustibles. Such products of combustion are typically carried significant distances away from the fire by convection and by the mine ventilation system.
4. Aerodynamic sensors respond to disturbances in the ventilation currents, such as might be caused by fire convection currents. However, these sensors are generally not sensitive enough to changes caused by fire unless they are located fairly close to the fire.
5. Hertzberg notes that the human observer is a combination of all of the detectors listed above. But the human detector has limitations with respect to sensitivity and location. A person can not detect products of

> combustion at levels as low as modern sensors, and people are not able to be present in some parts of mines – in particular, gob areas.

Sudhish Banerjee gives a recent summary of techniques for detecting coal mine fires, and assessing the status of coal mine fires. (Banerjee, 2000, pp. 148-169) He begins by saying that most of the approaches for developing fire detection devices are based on energy changes, such as flame detectors and temperature measuring devices; or material degradation of the fuel, such as smoke detectors or devices to measure chemical products of combustion. He notes limitations and disadvantages to all of the methods of coal mine fire detection.

Smith, Miron, and Lazzara, in a 1991 United States Bureau of Mines Report of Investigations titled “Large-Scale Studies of Spontaneous Combustion of Coal,” state that:

> “The analysis of gaseous products of combustion is the primary method used for the detection of spontaneous combustion in underground coal mines... The information does not show clear differences between safe conditions and the beginnings of heating events. Only in cases of advanced heating were the values from gas analysis more easy to interpret and able to identify heatings.” (p. 27)

Obviously, although considerable progress has been made in assessing mine fires, there are still problems – especially with the detection of concealed fires.

2.3.1 Detection of Concealed Fires by Physical Symptoms

Banerjee lists a number of physical symptoms that have been used as indicators of fire in concealed areas:

1. Haze in the air – which might be attributed to the initial stage of spontaneous heating driving moisture from the coal.
2. Sweating of the strata – that might be due to the condensation of moisture on the roof and ribs of a mine that is released from the heating of coal.
3. "Gob-stink," or "fire-stink" – a distinctive odor due to the heating of coal driving off organic distillates.
4. Sound – which might be due to the expansion, cracking, and falling of strata due to the advancement of fire.
5. Smoke – which Banerjee states can only be observed once a fire has become established.

He notes that all these physical symptoms have significant limitations. Haze and sweating of strata can be caused by changes in the temperature and humidity of ventilating air currents independently of the existence of any fire, yielding false, positive alarms. False negative results could result, depending on the mine environment and rate of heating. Gob stink, sound, and smoke cannot detect fire in the early stages. (Banerjee, 2000, pp. 148-149)

2.3.1.1 Fire Detection by Gob-Stink

Gob-stink can be listed as a physical symptom of fire, given that it is detected by the sense of smell, but gob-stink also presumably involves chemical degradation products of coal as it is heated. Chamberlain, Barrass, and Thirlaway conducted a series of experiments to study gob-stink using sensitive gas chromatographic techniques. They noted that coal oxidation reactions that begin even below ambient temperatures might produce chemicals, such as various organic acids, alcohols, aldehydes, and ketones, which would yield gob-stink odors. Such organic chemicals might be used as an earlier warning of coal oxidation and heating than other tests being used. However, detection of any of these chemicals would have to be accomplished by instruments to give an earlier warning than a human could give, because prior work cited indicated that the lowest temperature of oxidation that could be detected by a human's sense of smell was about 120° C. (Chamberlain et al, 1976, p.220). These authors conducted oxidation tests on three different coals. They used varying concentrations of oxygen mixed with nitrogen and varied the temperature of the reaction from 13° C to 127° C. They noted that acetaldehyde and methyl alcohol were produced at lower temperatures than carbon monoxide at the 0.01 ppm (parts per million) level, but at the 0.1 ppm level, carbon monoxide was produced at the lower temperature. At all higher levels of detection, carbon monoxide was always produced in greater quantities at lower temperatures than any of the organic gases that were tested for.

This fact concerning production of carbon monoxide versus organic compounds, that would be components of gob-stink, raises questions concerning current efforts to substitute for human noses so called "electronic noses." Some researchers are currently trying to develop semiconductor sensors – electronic noses – that might measure organic compounds in a mine atmosphere at sub-ppm levels. For example, Reimann and Schutze are working on a multi-detection system of sensors to measure carbon monoxide and ethene. (Reimann & Shhutze, 2012) However, if carbon monoxide is generated in greater quantities at lower temperatures, monitoring for other fire gases may serve only to confirm a condition that is already known from very high carbon monoxide measurements.

2.3.1.2 Fire Detection by Smoke

The term "smoke" may need some further explanation. As visible particles, the presence of smoke would indicate a well developed fire, as mentioned above. However, some research has indicated that detection of smoke as sub-micron particles by ionization type smoke alarms may offer a warning of fire earlier than carbon monoxide detectors. (Conti & Litton, 1992) However, ionization type smoke alarms have not actually seen widespread use in any mine – certainly not for guarding against concealed fires.

2.3.2 Detection of Concealed Fires by Products of Combustion

Currently, the principal method of fire detection in coal mines in the United States involves monitoring CO levels in the mine atmosphere. This approach is based on studies that have shown that CO is not present in unmined coal seams, but is produced by ambient temperature oxidation of the coal once the coal is exposed to air, and is produced in ever greater quantities as spontaneous combustion, or an incipient fire, is developing.

Before examining the different gas tests that have been developed to try to aid in the determination of a concealed fire, it is important to become familiar with the different gases which different coal seams can give off naturally, and with other sources of contamination of a coal mine atmosphere without development of a fire.

2.3.2.1 In Situ Gases in Coal Seams

Kim, in the United States Bureau of Mines Report of Investigation Number 8317, published in 1978, states that carbon monoxide does not occur in coal seams that have not been exposed to air by mining. (Kim, 1978, p. 12) This Bureau of Mines Report is a summary of work that Kim initially reported in more detail in 1973, in the Bureau of Mines Report of Investigations Number 7762 in which she gives an account of the in situ gas composition of seven different coal seams.

In the more detailed 1973 report, Kim used gas chromatography to determine whether or not some common gases, including some light weight hydrocarbons, were present in situ in coalbeds. Gas samples were collected directly from horizontal and vertical boreholes that were drilled into coal seams for methane degassing, by placing the ends of large (250ml) evacuated gas sampling bottles into the boreholes and breaking the tip of the bottle. She noted that air contamination was a serious problem; and that generally, a sample that contained more than eight percent nitrogen and two percent oxygen was considered to be highly contaminated and was not included in calculations of gas composition.

Multiple samples were collected and analyzed from the following coal seams:

1. Pocahontas No. 3; Buchanan County, VA
2. Pittsburgh; Greene and Washington Counties, PA; Marion County, WV
3. Upper Kittanning; Cambria County, PA
4. B Seam, Mesaverde Formation; Pitkin County, CO
5. Lower Hartshorne; LeFlore County, OK
6. Mary Lee; Jefferson County, AL

The results of the analysis from a number of samples collected from these coal seams are briefly summarized in Table 2. Kim's report gives much more detail.

Table 2

Measurements of Various In Situ Gases from Selected Coal Seams

CH_4 = methane, C_2H_6 = ethane, C_3H_8 = propane, C_4H_{10} = butane, CO_2 = carbon dioxide, O_2 = oxygen, N_2 = nitrogen, H_2 = hydrogen
(Kim, 1973, pp. 3-5)

Coal Seam	**CH_4**	**C_2H_6**	**C_3H_8**	**C_4H_{10}**	**CO_2**	**O_2**	**N_2**	**H_2**
Pocahontas No. 3	97.61-63.1	1.59-0.85	0.0109-0.0	0.0013-0.0001	0.57-.06	0.31-0.04	35.96-0.70	0.02-0.0
Pittsburgh	95.86-84.4	1.08-0.04	0.0	0.0	14.75-2.54	0.5-0.04	1.2-0.05	0.0
Upper Kittanning	99.17-95.47	0.02-0.0	0.0	0.0	0.18-0.0	0.47-0.0	3.97-0.64	0.0
B Seam, Mesaverde Formation	87.84	0.05	0.0046	0.0011	11.99	0.0	0.09	0.0
Lower Hartshorne	99.22	0.01	0.0	0.0	0.06	0.1	0.6	0.0
Mary Lee	96.05	0.01	0.0	0.0	0.1	0.05	3.5	0.27

As shown in Table 2, methane was always the most prevalent gas, but the amount of methane measured was not always consistent even within the same seam. The Pocahontas No. 3 seam had three measurements for methane that were in the range of 96 to 97 percent methane, but one measurement of methane that was only 63.1 percent. The sample with the low methane reading had an unusually high measurement for nitrogen of 35.96 percent. Kim noted that this high nitrogen reading could not be attributed to contamination, in part because the oxygen measurement was 0.0 percent for this sample.

Similarly, of four samples analyzed from the Pittsburgh coal seam, two had readings for methane of 95.86 and 93.85 percent while two had significantly lower readings for methane of 88.91 and 84.4 percent. The two lower readings were basically offset by much higher readings for carbon dioxide of 10.97 and 14.75 percent respectively, as opposed to carbon dioxide readings of 2.54 and 4.75 percent respectively in the other samples.

Not reproduced in the simplified Table 2, but noted by Kim, is that two coal seams produced measurable amounts of helium. The Pocahontas No. 3 seam produced between 0.02 to 0.05 percent helium (three different samples), whereas the Mary Lee seam produced 0.27 percent helium (one sample). Kim noted that the presence of helium in coal is attributed to radioactive decay.

Finally, as noted in Table 2, all the seams produced some ethane, and a few of the seams produced some propane and butane. The Pocahontas No. 3 seam produced the highest ethane readings, with the highest reading of four samples at 1.59 percent. (Kim, 1973, pp. 3-5)

Kim and Douglas, in a subsequent paper, reported on gas chromatographic analysis of five different coal seams than the coal seams listed above, with similar results. Methane, ethane, propane, hydrogen, and carbon dioxide were present, but the different gas measurements varied significantly even within the same seam. (Kim and Douglas, 1973).

As will be shown below, some of these gases that are naturally evolved from coal seams could be confused with gases given off during the oxidation of coal, or could alter gas measurements that are used to construct so called fire indices. Either way, confusion in interpretation of fire indicators could result in false conclusions about the existence of a concealed fire. Especially problematic is the fact that very different gas emissions can result from the same coal seam over fairly small distances in the seam.

2.3.2.2 Other Sources of Contamination

Alterations of mine atmospheres that could cause misinterpretations of gas readings are not limited to coal seam emissions. Banerjee discusses various contributors to the composition of mine atmospheres, noting that although normal air typically contains 79.04% of nitrogen (and inert gases), 20.93% of oxygen, and 0.03% of carbon dioxide; conditions existing in a coal mine can alter and adulterate normal air. He not only notes adulteration of mine atmospheres by gases given off by the coalbed, but he also lists other sources of contamination. For example, oxygen levels can be reduced by breathing, combustion, and coal oxidation. Nitrogen levels can be increased by any of the factors that reduce oxygen levels, and, on occasion, by emissions from strata. The amount of carbon dioxide in a mine atmosphere can be increased by exhaled air, coal oxidation, acid mine water reacting with carbonates, timber decay, and emissions from strata. Furthermore, carbon monoxide can be introduced into a mine atmosphere by oxidation of the coal at ambient or elevated temperatures, shot-firing operations, or by diesel equipment. And, as already noted, methane and other unsaturated hydrocarbons can be introduced by emissions from strata, as well as by distillation from heated coal. (Banerjee, 2000, pp. 154-156)

2.3.2.3 Fire Indices

There have been a number of fire indices proposed over the last century. These fire indices are various gas measurements, or ratios of different gas measurements, that have been developed by various investigators in order to try to determine whether or not a fire exists in a coal mine – especially in an inaccessible area.

Banerjee (2000, pp. 156-168) discusses a number of these fire indices. His discussion is generally brief. Mitchell (1996), principally in a chapter titled “Interpreting the State of the Fire,” discusses in some detail numerous gas readings and ratios that are in use. Several United States Bureau of Mines publications, including “Diagnostics of Sealed Coal Mine Fires” by Kutchta, Furno, Dalverny, Sapko, and Litton (1982); and several other recent publications, including Panigrahi and Bhattacherjee’s 2004 paper titled “Development of Modified Gas Indices for the Early Detection of Spontaneous Heating in Coal Pillars,” describe a number of fire indices. Naturally, there exists considerable overlap in the coverage of the different fire indices; however, between these, and a few other publications, the most common and enduring fire indices can be determined. No single publication mentions every one of the commonly used indices. The measurements and ratios that appear to have been considered, and used, the most are listed below:

1. Graham’s Ratio
2. Carbon Dioxide – Oxygen Deficiency Ratio
3. Willet’s Ratio
4. Unsaturated Hydrocarbons
5. Oxygen Consumption
6. Carbon/Hydrogen Ratio

7. Jones and Tricket Ratio
8. Carbon Monoxide/Carbon Dioxide Ratio
9. RATIO
10. Morris
11. Carbon Monoxide Trend

2.3.2.3.1 Graham's Ratio

Graham's Ratio is also known as the "Index for Carbon Monoxide," or "ICO." Sometimes this ratio is also referred to as the "carbon monoxide – oxygen deficiency ratio." Graham introduced the ratio in a paper in 1921, in which he reported that there was a relationship between how much oxygen was consumed in an oxidation reaction of coal, the carbon monoxide produced by the oxidation, and the temperature at which the oxidation occurred. This relationship is written as a ratio, or formula, in various ways – usually in one of the following three forms:

$$\frac{\mathrm{CO}}{\Delta \mathrm{O_2}} \tag{1}$$

$$\frac{\mathrm{CO}}{\mathrm{O2-deficiency}} \tag{2}$$

$$\frac{\%\mathrm{CO}}{\left[(0.265)(\%\mathrm{N_2})-(\%\mathrm{O_2})\right]} \tag{3}$$

The last way in which the formula is written above actually indicates how it is typically calculated. For example, in the case of an inaccessible gob, an assumption is made that oxygen was present in the air that entered the gob in the same proportion to the amount of nitrogen as would be true for ordinary air. The concentration of oxygen in ordinary air is typically about 20.93%, and the concentration of nitrogen in ordinary air is about 79.04%, therefore the ratio of these two gases in ordinary air is about 0.265. So, if the percent of nitrogen is determined in the air exiting the gob, and multiplied by 0.265, the equivalent amount of oxygen that would be in undiluted air is calculated. This number can then be compared to the measured amount of oxygen exiting the gob, and the difference represents how much oxygen was consumed in an oxidation reaction. Of course, this calculation would simply return a value of 20.93 if the original air entering the gob were in no way diluted with any other gases. Under such a circumstance, one could as easily enter 20.93 into the first value in the denominator of the equation. This is what Graham did originally. However, in a typical gob, the original air will be diluted by other gases, such as methane. As long as nitrogen is neither added nor subtracted from the original air, using nitrogen as a reference avoids the dilution problem. Then, by subtracting the measured percent of oxygen exiting the gob from the percentage of oxygen that should have been in the air exiting the gob if there had been no oxidation reaction, one derives how much oxygen was used – the oxygen deficiency. Dividing the percentage of carbon monoxide in the exiting gas by this oxygen deficiency gives one the “Graham’s Ratio.”

This ratio is based on the assumption that nitrogen is neither added to nor subtracted from the air that is involved in any fire scene, and that any dilution of any of the component gases of the numerator or the denominator, by methane or additional air, will affect both the numerator and denominator equally and therefore be offset.

Graham observed, by numerous laboratory experiments, that his ratio gave higher numbers for reactions where the temperature of the oxidation of coal was higher. On this basis, he proposed that this relationship could be used to tell whether or not spontaneous combustion was occurring in an inaccessible area. (Graham, 1921, p. 231)

Mitchell mentions that in many mines, Graham's Ratio is used for monitoring for spontaneous combustion. He states that this technique has two serious problems – it gives lower values and less obvious trends where:

1. Air flows from an area of spontaneous combustion are diluted by other sources of air before measurement, and
2. Air passes through an area that contains less than the normal amount of oxygen – typically due to production of blackdamp. (Mitchell, 1996, p. 31)

Mitchell also cautions that there are other potentially serious problems with the use of this ratio. In particular, Mitchell (1996, p. 83) warns against using Graham's Ratio when:

1. Carbon monoxide could be present from other sources than the fire; or,
2. $\Delta O_2 < 0.3$, which would equate to a ratio far higher than would be theoretically possible.

In addition, Mitchell points out that carbon monoxide is readily adsorbed by cokes and soot, absorbed by wet coal, and consumed by some fungi; all of which could introduce inaccuracies to gas readings. (Mitchell, 1996, p. 71)

Mitchell's warnings about the limits for using Graham's Ratio are accented in a case study on the use of this ratio, and other ratios, by Panigrahi and Bhattacherjee (2004); who examined efforts to detect spontaneous combustion in coal pillars in an Indian coal mine. These authors observed that most cases of spontaneous combustion in coal pillars occurred within two to three meters of the surface of a pillar that had a high ventilation pressure difference across it. They drilled boreholes 3.5 meters deep into pillars that were subjected to high pressure differentials, and took gas samples from the inside of these pillars on a weekly basis. On the basis of the samples, calculations of Graham's ratio (and other ratios that rely on a calculation of oxygen deficiency) frequently gave negative – clearly meaningless – numbers. Because they were drilling holes into a pillar in a gassy seam, the majority of the gas in most of their samples was methane. They speculated, but offered no supporting evidence, that as methane was desorbed from the coal of the pillar, nitrogen filled the vacated pore spaces. This resulted in a nitrogen deficiency in the samples, which meant that the oxygen deficiency did not equal $\{(0.265)(\%N_2) - (\%O_2)\}$, as per Mitchell's caution. Panigrahi and Bhattacherjee (2004, pp.371-373) then proceeded to suggest that an appropriate adjustment to Graham's Ratio could be made by recalculating the gas percentages on a methane free basis, ignoring the fact that such a calculation does not adjust for any "lost" nitrogen that results in the calculation problem described above.

Banerjee notes that Graham published several papers in the time period of 1914 to 1930 on the importance of monitoring carbon monoxide and carbon dioxide levels in mine atmospheres, and described how observing the amounts of carbon monoxide and carbon dioxide produced with respect to the amount of oxygen consumed could be used to determine the degree of heating taking place in a coal mine. He states that Graham concluded, in a 1930 paper, that the early detection of the heating of coal could be best be accomplished by use of the CO/O_2-deficiency ratio, now known as Graham's ratio; whereas the subsequent progression to actual fire was best indicated by CO_2/O_2-deficiency ratio. (Banerjee, 2000, p. 158)

Singh et al. (2007) note that readings and ratios of carbon monoxide can sometimes give false readings because the amount of carbon monoxide can decrease, even in a sealed area. Banerjee, Nandy, and Chakravorty, in a paper titled "Studies in the Mode of Disappearance of CO Over Coal in Sealed Off Area in Mines," published in 1965, attributed this disappearance to bacterial action. As already noted above, Mitchell attributes the disappearance of CO to adsorption.

Chakravorty and Woolf, in a paper presented at the Second International Mine Ventilation Congress, concluded that:

> "The system based on the continuous monitoring of carbon monoxide in mine air appears to be a satisfactory and practical method for the early detection of heating. The absolute level of carbon monoxide in the mine air, whether high or low, is not of great significance but an increasing trend over a period is indicative of heating." (Chakravorty and Woolf, 1980, p. 435)

They discount the necessity of using Graham's ratio, or any ratio. Their concern is based on the ability of measuring the nitrogen and oxygen content of the mine air well enough to be able to calculate a meaningful number for any ratio that is dependent on any of those values. They note that there still appeared to be problems measuring nitrogen to the necessary limits of ±0.01%. They continue by citing work done at the Somerset mine in Colorado that demonstrated that using Graham's ratio did not prove to be any better than monitoring the trend of the carbon monoxide concentration in the mine atmosphere. They do not address any of the concerns listed above concerning adsorption/absorption or variable dilution of carbon monoxide. (Chakravorty and Woolf, 1980, 429 – 430)

Furthermore, one of the more recent articles that examines the production of CO_2, and CO, as well as water (H_2O), published in 2002 by Wang, Dlugogorski, and Kennedy, raises additional questions about relying on carbon monoxide production. These authors noted that coal oxidation at low temperatures yields both solid and gaseous products. The solid products consist of oxygenated radicals on the carbonaceous surface of the coal, and the gaseous products are, for the most part, CO_2, CO, and H_2O. The authors contended that no mass balance for coal oxidation using an isothermal flow reactor had ever been done, so they conducted such tests at various temperatures and oxygen concentrations in a gas stream. They concluded that, at temperatures between 60 and 90 °C, CO_2 is produced in greater quantities than CO with a molar ration of three to one. Water is produced proportional to CO production, with a molar ratio of 21 H_2O/CO. Furthermore, the mass of the coal samples increased – more than offsetting the mass that would be lost due to some of the carbon being removed to form the gaseous products. Finally, Wang et al. concluded that the molar ratio of CO to O_2 consumed depends on the temperature and, naturally, on the oxygen concentration. They point out that the dependency of CO production on O_2 concentration means that any index involving CO may be of questionable reliability, given that O_2 concentrations can, and do, vary in coal mines – especially if a fire is involved.

2.3.2.3.2 Carbon Dioxide – Oxygen Deficiency Ratio

The Carbon Dioxide – Oxygen Deficiency Ratio is similar to Graham's Ratio, with the obvious difference that the numerator of this ratio is CO_2 rather than CO. As with Graham's Ratio, the formula can be written several different ways:

$$\frac{CO_2}{\Delta O_2} \tag{4}$$

$$\frac{CO_2}{O_2 - \text{deficiency}} \tag{5}$$

$$\frac{\%CO_2}{[(0.265)(\%N_2) - (\%O_2)]} \tag{6}$$

In some papers, this ratio has been referred to as "Young's Ratio."

Graham not only studied the ratio of carbon monoxide to oxygen consumed – $CO/\Delta O_2$; he also studied the equivalent ratio for carbon dioxide – $CO_2/\Delta O_2$. In a paper published in 1930, he observed that the $CO_2/\Delta O_2$ ratio was greater during the early stages of oxidation at low, constant temperatures than during later periods of time in the same experiment. He was able to attribute this to the evolution of carbon dioxide that was adsorbed by the coal. On the other hand, he noted that carbon monoxide always showed an increase with time and with temperature; and accordingly, he recommended that the $CO/\Delta O_2$ ratio was a better indicator of the initial heating due to the development of spontaneous combustion; while the $CO_2/\Delta O_2$ ratio was the best indicator of the transition from heating to actual fire. (Graham, 1930)

In 1991, Smith, Miron, and Lazzara of the Bureau of Mines, published the United States Bureau of Mines Report of Investigations Number 9346 in which they concluded that the $CO_2/\Delta O_2$ ratio was the only ratio, of four ratios that they examined, that gave an early warning of spontaneous heating. The four ratios they examined were the Graham's ratio, the $CO_2/\Delta O_2$, the CO/CO_2 ratio, and an "R ratio." The R ratio is a ratio developed by Litton in the Bureau of Mines Report of Investigation 9031 (see "RATIO" below). The CO/CO_2 ratio is discussed below. Smith et al. conducted their tests in a specially constructed test chamber with an input of very controlled air that was not adulterated by any of the contaminants that might be routinely found in coal mine air (Smith et al, 1991, pp. 3-5). They noted that CO_2 has different potential sources in a coal mine, making the use of CO_2 unreliable (Smith et al, 1991, p.27). They offered no conclusions about how problems with CO_2 measurements might affect the reliability of the $CO_2/\Delta O_2$ in a real mine setting.

Mitchell discusses the use of CO_2 detectors and potential problems with CO_2 measurements. He states that CO_2 production is as much as 100 times greater than CO production in the earliest stages of spontaneous combustion – at temperatures below 100 degrees Celsius. However, he notes that there are potential problems with trying to use CO_2 measurements to monitor for fire:

1. Areas of dripping, flowing, or pooled water will absorb CO_2, yielding misleadingly low CO_2 readings,
2. Acid waters can react with calcium carbonates in shale, that is associated with the coal, producing misleadingly high CO_2 readings, and
3. Blackdamp formation will give misleadingly high CO_2 readings (Mitchell, 1996, p. 31).

2.3.2.3.3 Willet's Ratio

H. L. Willett, in 1951, published an article titled "The Interpretation of Samples From Behind Stoppings with a View to Reopening." In this article, he observed that in some situations Graham's Ratio did not give an accurate indication as to the state of a possible fire in a sealed area. (It might also be noted that Willett observed that Graham had never actually proposed that his ratio could be applied to the evaluation of sealed areas.) Specifically, in some mines, levels of CO did not decline even after there was no longer any fire. Therefore, one would still calculate a high Graham's Ratio that normally would be indicative of a fire when, in fact, the fire would have been smothered by the sealing. For some mines, CO levels do drop in a sealed area after a fire is extinguished. For those mines, Willett maintained that Graham's ratio was still the best indicator of extinguishment.

Willett contended that for mines in which Graham's ratio would not work, another ratio was needed. He described how he first considered some measure based on the trend of the CO_2 in the blackdamp, but observed that such wide fluctuations occurred, that a trend based on whether or not conditions in sealed-off areas were normal was not possible. After analysis of samples obtained from a large number of mined-out areas under normal conditions, Willet concluded that "it appeared to be very evident that some of the carbon dioxide had been given off from the strata in association with the combustible gas." (Willett, 1951, p. 638) This fact seemed to account for the fluctuations in the CO_2 in the blackdamp. He then compared a number of gas readings from different sealed areas and noticed that there appeared to be a correlation between the ratio of the CO_2 as a percentage in the blackdamp in a sealed area, and the percentage of combustible gas in the same sealed area. Based on these observations, Willett concluded that he should study trends in the amount of CO_2 in the blackdamp plus the combustible gas. He ultimately concluded that he could determine whether or not a fire in a sealed area, in which CO levels did not disappear, was extinguished by observing trends, in a sealed area, of the ratio – now known as “Willett’s Ratio”:

$$\frac{\text{CO}_2\ \text{Produced}}{\text{Blackdamp} + \text{Combustible Gas}} \tag{7}$$

Banerjee emphasizes that Willet’s ratio is a supplemental ratio that is only applicable in particular cases where it is observed that for gas samples collected from sealed off fire areas, the CO does not disappear, but declines at a slow rate – apparently with the gradual extinction of a fire. Banerjee notes that this ratio, as Willet proposed, is to be used in conjunction with CO readings that would confirm that the CO concentration is in an appropriate trend. With this appropriate circumstance, Willet’s ratio could be used to determine the extent of the fire. (Banerjee, 2000, p. 160)

Panigrahi and Bhattacherjee (2004) studied the use of Willet’s Ratio and determined that, under certain circumstances, its use would give erroneous results. Specifically, they list gas measurement data for carbon monoxide, carbon dioxide, oxygen, and methane taken from holes bored in coal pillars; and they list corresponding calculated values of Willet’s ratio and four other ratios. They demonstrated, with these calculations, that for gas mixtures that contain high percentages of methane, calculations of Willet’s ratio give numbers that are not meaningful.

Because this ratio involves carbon dioxide, the same cautions mentioned at the end of the above section on the Carbon Dioxide – Oxygen Deficiency Ratio apply here too.

2.3.2.3.4 Unsaturated Hydrocarbons

In a Bureau of Mines Report of Investigation Number 7965, Kim studied short-chained hydrocarbon gases that were given off by coal samples at three different temperatures. Coal samples from six different seams were heated at constant temperatures of 35, 125, and 150 degrees C. She noted that at 35°C, 99 percent of the hydrocarbon gas evolved was methane, whereas at 125°C and 150°C, methane constituted only about half the hydrocarbon gas evolved. (Kim, 1974)

Banerjee summarized several different authors' works that examine the production of different saturated and unsaturated hydrocarbons from coal that undergoes increasing heating. He notes that several papers appeared in the time period of 1959 to 1964 that examined the production of ethane (C_2H_6), ethylene (C_2H_4) and acetylene (C_2H_2); and similar organic compounds. Banerjee credits T. Kittagowa with first proposing in 1959 that olefins, such as ethylene, in conjunction with CO, could be better indicators of spontaneous combustion than carbon monoxide alone. Banerjee also cites B. R. Pursall and S. K. Ghosh, who in a 1963 paper reported on the analysis of mine air samples using gas chromatography. They observed that: in order; ethylene, propylene, and acetylene were produced in increasing amounts by the heating of coal. (Banerjee, 2000, pp.160-161)

However, later work in the 1970's by Chamberlain, Hall, and Thirlaway established that carbon monoxide is emitted earlier, and in greater quantities, than the unsaturated hydrocarbons, as coal is progressively heated. These authors conducted tests on samples from 17 different seams of British coals, ranging in rank from lignite to anthracite, by exposing the different coals to gradually increasing temperatures, while flowing either nitrogen or dry air through the samples. Temperatures were gradually raised from 16°C to 248°C for each of the samples. For each of the 17 different seams, a sample was exposed to increasing temperatures with dry air flowing through it, and then in another experiment, with nitrogen flowing through it. Exit flows were analyzed for different gases, and any gases detected from the experiment with nitrogen flow were attributed to gases desorbed or distilled from the coal. Any gases detected in the exit flows from the dry air experiment that were not present in the nitrogen experiment were attributed to oxidation. They concluded that carbon monoxide is a more sensitive indicator, compared to other proposed gases such as hydrogen and ethylene, of the heating of coals that could lead to spontaneous combustion. They summarized their conclusions concerning the production of carbon monoxide, hydrogen, ethylene, and propylene, and the possible use of these gases as indicators of spontaneous combustion, in a number of figures, including a figure that is reproduced here as Figure 1.

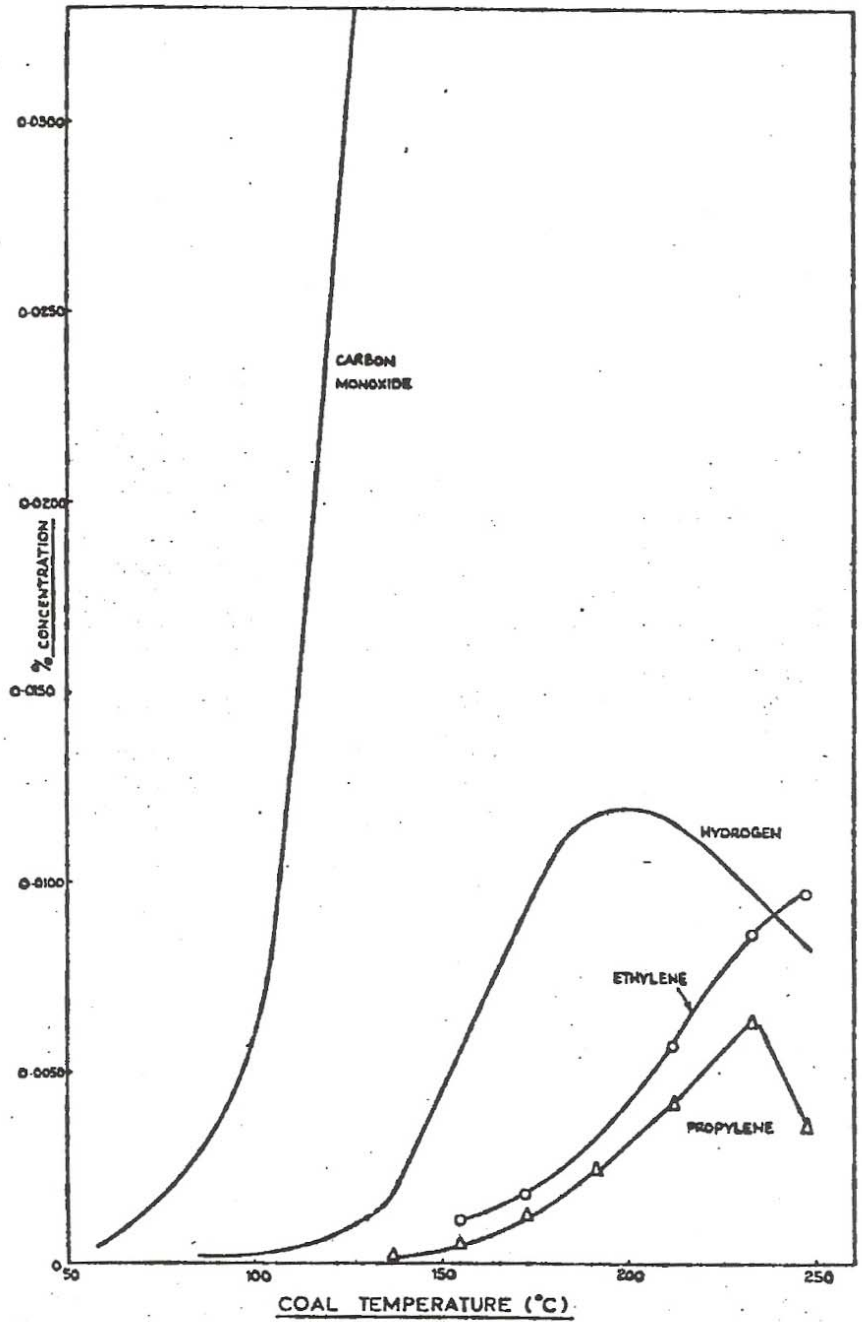

Figure 1
Dynamic Oxidation Tests: Westoe Five-Quarter Coal in Dry Air Only: Gas Concentration versus Temperature.
(Chamberlain et al.,1970, p.13, Figure 8)

2.3.2.3.5 Oxygen Consumption

Banerjee states that there is currently no definitive test that would indicate whether or not a sealed fire is “extinct.” He defines extinct to mean that the sealed fire is sufficiently dormant that when air is reintroduced into the sealed area, the fire does not rekindle – at least in a time period necessary for the fire area to be recovered. He discusses the use of oxygen consumption as a way of telling if a fire is extinct. A fire in a sealed area can smolder, and remain relatively hot for a long time, even in a very low oxygen concentration of only one or two percent. If the sealed area is reopened too soon, the fire will rekindle. Banerjee quotes a paper by Gupta and Bagchi titled “Significance of Air Composition in Sealed Mines in Relation to the Time of Their Reopening,” published in 1970, as indicating that an oxygen consumption rate of less than 0.0007 percent per day indicates that a sealed fire is extinct. However, he notes that: “it is extremely difficult to ascertain oxygen consumption rate accurately, in an actual fire area kept sealed, because of the uneven leakage of air within it.” (Banerjee, 2000, pp. 162-163)

2.3.2.3.6 Carbon/Hydrogen Ratio

Banerjee discusses a “carbon/hydrogen ratio” that was the subject of a paper Ghosh and he authored in 1967. This ratio is calculated based on the formula:

$$\frac{C}{H} = \left\{ \frac{6\left[CO_2 + CO + CH_4 + 2(C_2H_4)\right]}{\left[0.265N_2 - O_2 - CO_2 + C_2H_4 + CH_4\right]} \right\} + H_2 + CO \tag{8}$$

This formula was derived by considering coal to be a fuel with a general composition of $C_xH_yO_z$, and stoichiometrically oxidizing it. The largest C/H value for the complete burning of bituminous coal is between 16 and 20. Higher values would indicate burning of timbers while lower values would indicate the incomplete burning of coal. Banerjee contends that from C/H ratios, along with the consumption of CO_2, one can deduce the degree of the burning of coal, and the size of the fire. However, he acknowledges that there are limitations to the use of this ratio (Banerjee, 2000, pp. 163-165):

1. Unlike some other ratios, such as Graham's ratio, the C/H ratio is not independent of dilution with CH_4 from the strata.
2. Any source of CO_2 other than combustion of fuel, and any potential loss of CO_2, such as dissolution in water will affect the accuracy of the calculation.
3. Air leakages can adversely affect the calculation of the rate of O_2 consumption.

2.3.2.3.7 Jones and Trickett Ratio

John H. Jones and J. C. Trickett published a paper in 1954 that suggested that, after a coal mine explosion, the principal constituent of the explosion – methane or coal dust – could be ascertained by studying the amount of different gases produced. (Jones & Trickett, 1954, pp. 768-791) Based on theoretical consideration, they derived a formula that would apply to a stoichiometric equation for the complete combustion of methane with oxygen to produce only carbon dioxide, carbon monoxide, hydrogen and water. They expressed this formula as:

$$\frac{CO_2 + 0.75CO - 0.25H_2}{O_2} = 0.5 \qquad (9)$$

The items in the numerator are in terms of volumes of the gases produced, and the denominator is in the term of volume of gas consumed.

Jones and Trickett then made some additional points about this equation:

1. The volume of oxygen used can be calculated from the nitrogen content of the combustion products (as with Graham's ratio), and is referred to as the "oxygen deficiency." The denominator is then expressed as:

   $$\{0.265(N_2)-(O_2)\}$$

   The equation can then be written in a more common form:

   $$\frac{[(CO_2)+0.75(CO)-0.25(H_2)]}{[0.265(N_2)-(O_2)]} \tag{10}$$

2. Any dilution of the product gases with air or methane will not affect the value of the ratio.
3. Additional products of combustion than those in the equation have been detected. To the extent that other products are formed, such as carbon (soot), ethane, ethylene, etc., the formula above will not be equal to 0.5, but will be somewhat less than 0.5.

In a similar manner to the case for methane, through basic chemical reasoning, Jones and Trickett then examined the reactions for a coal dust explosion; and concluded that the above formula would be equal to, or slightly greater than 0.85, rather than 0.5. As might be imagined, there were some stipulations:

1. This relation for a coal dust explosion will be correct if there is not a significant amount of unburnt carbon. Unburnt carbon will reduce the ratio.
2. Approximately three-quarters of the coal taking part in the explosion would have to be converted to carbon, rather than oxidation products, for the ratio to be reduced to 0.5.

Banerjee notes that several researchers have attempted to use this ratio for mine fire diagnosis without much success. Values ≤0.5 would correspond to a methane explosion, whereas values around 0.85 ±0.18 would indicate a coal dust explosion. (Banerjee, 2000, p. 165) Banerjee does not explain or reference this last statement with the value of “0.85 ±0.18.” Jones and Trickett do not mention the ±0.18 in their original paper.

Kuchta et al (1982) studied the Jones – Trickett Ratio as a potential indicator of the state of a coal mine fire. They note also that this ratio was originally developed to determine if an explosion was caused by methane or coal dust, and was not meant to be used as a determinant of the state of a mine fire. However, because it has been used by other investigators to try to monitor mine fires, these authors examined this ratio to see how it would respond to their large-scale, sealed fire tests. They summarize the expected values for the ratio as follows:

1. 0.5 for complete combustion to carbon dioxide.
2. Greater than 0.5 for other hydrocarbons, depending on the Hydrogen to carbon mole ratio.
3. 0.5 to 1.0 for coal.
4. Equal to, or greater than 1.0 for wood.

A typical chart of the calculated values of the Jones – Trickett Ratio for one of the tests is shown in Figure 2.

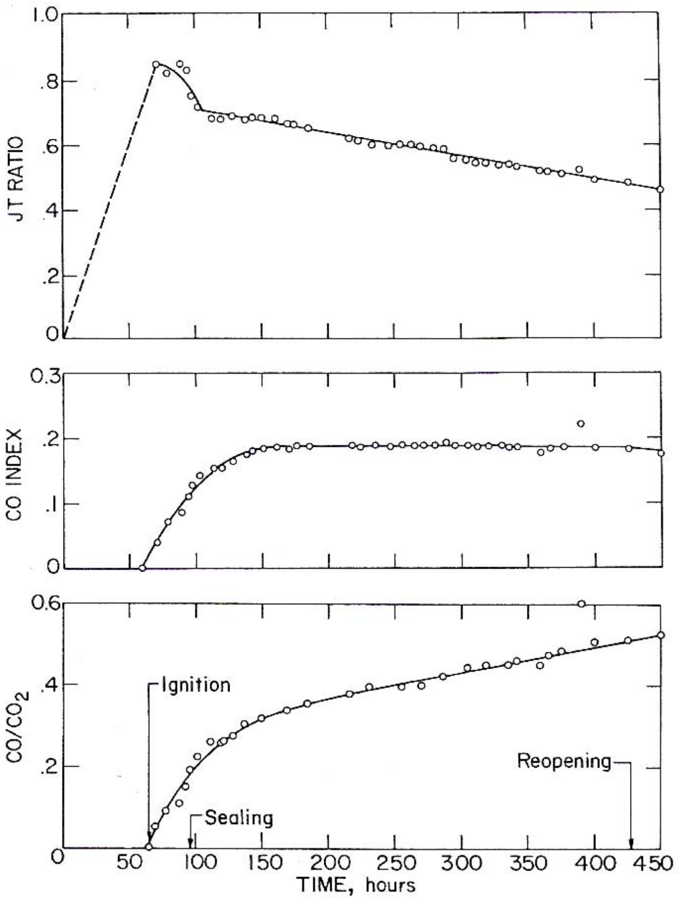

Figure 2
Graphs Showing the Trend of 3 Common Fire Indices vs Time
(Kuchta et al, 1982, p. 21, Figure 20)

They concluded that "a ratio noticeably less than 0.5 in a coal mine fire could be indicative of extinguishment or greatly reduced coal temperatures." (Kuchta, et al, 1982, p. 19)

Mitchell recommends using the Jones – Trickett Ratio for two different purposes. First, he describes using the ratio to check on the reliability of samples and analyses. If a sample of mine air, drawn to check on whether or not a fire exist in a mine, has a calculated Jones – Trickett value of greater than 1.6, the sample should be rejected. If coal is the principal fuel for the fire, and a lot of timber in the fire area is unlikely, any calculated value for the ratio is suspect. (Mitchell, 1996, p.64) Second, Mitchell states that the Jones – Trickett Ratio can be used to determine the probable principal fuel of a fire. If the ratio gives a value of less than 0.6, methane is the probable fuel. Coal is the probable fuel if the ratio is between 0.6 and 1.0, while wood is the probable fuel if the ratio is above 1.0. (Mitchell, 1996, p.97) Obviously, all the cautionary statements in earlier sections concerning the measuring of oxygen, carbon dioxide, and carbon monoxide concentrations from inaccessible areas of coal mines would apply.

2.3.2.3.8 Carbon Monoxide/Carbon Dioxide Ratio

Banerjee states that “Thermodynamically and from gasification point of view, CO/CO_2 ratio of products of combustion may be considered to attain an equilibrium in a particular combustion situation.” (Banerjee, 2000, pp. 165-166) Banerjee recognizes that this ratio has the same limitations as any measurement or ratio involving carbon dioxide – extraneous sources of carbon dioxide, such as blackdamp; and the possible loss of carbon dioxide, as with dissolution in water

Kuchta et al, in the 1982 Bureau of Mines Report of Investigations Number 8625 titled “Diagnostics of Sealed Coal Mine Fires,” report on the results of four different sized test coal fires that were conducted at the Bureau of Mines test mine at Bruceton, Pennsylvania. These authors examined the products of combustion, and some related gas ratios, for test fires that varied in size from 4000 to 21,000 pounds of rubblized bituminous coal. These fires were ignited and allowed to become established, and then sealed. Oxygen, carbon monoxide, carbon dioxide, methane, and hydrogen concentrations were measured for the different fires from the time of ignition up to a time that the different fires were unsealed – which varied between 190 to 427 hours. One of the gas ratios studied was the CO/CO_2 ratio. These authors state that;

> “This ratio indicates the completeness of the combustion or oxidation and is defined in terms of volume-percent concentrations of CO and CO_2 that are formed. The ratio is «1 in a lean coal-air fire and varies with coal temperature and the oxygen concentration of the atmosphere.”

The temperature history, gas concentrations, and various gas ratios were plotted versus time for the four different coal fires. The plot for one of the fires is reproduced above as Figure 2. These authors concluded that the CO/CO_2 ratio is a more sensitive indicator for determining the state of a coal mine fire then is the $CO/\Delta O_2$ ratio because the CO/CO_2 ratio is more sensitive to temperature. However, they concluded that neither ratio was really very useful for determining the status of a sealed fire because neither ratio varied much after most of the oxygen in the sealed system was consumed. (Kuchta et al, 1982, pp. 12-24)

Mitchell recommends that “until practical, dependable means for detection of spon com are demonstrated, the miner’s best bet is to monitor the CO/CO_2 ratio.” (Mitchell, 1996, p. 31) In particular, he recommends taking measurements, and watching for trends to develop, at different places in a mine. He explains that this ratio will not be adversely affected by dilution, and generally a trend will not be adversely affected by water or acids depleting or increasing CO_2 amounts, as is the case with the monitoring of CO_2 by itself. As heating in an area of spontaneous combustion increases, the CO/CO_2 ratio should increase. Finally, he notes that monitoring this ratio may be impractical or questionable in some cases, in which case he recommends following the trends of a number of key gases, in particular nitrogen, oxygen, CO, and CO_2 (Mitchell, 1996, p. 32)

2.3.2.3.9 RATIO

Charles Litton, in a 1986 United States Bureau of Mines Report of Investigation titled “Gas Equilibrium in Sealed Coal Mines,” developed a ratio of gases to try to determine when an area that had been sealed due to a fire was safe to reopen. Litton referred to his ratio as “RATIO.” Others have referred to it as “Litton’s Ratio,” or “Carbon Monoxide – Residual Gas Relationship,” or “R-Index.”

Litton does define an R-Index, which he denotes as “R_I,” but this R-Index is just one step in his development of the RATIO. The R-Index is defined as:

$$R_I = \left| d(CO)\frac{R_g}{d(R_g)} \right| = 100\left[\frac{CO_s}{(R_g)^2} \right] \tag{11}$$

In this equation, CO_s is equal to the concentration of carbon monoxide in an original sample of a sealed mine atmosphere, in parts per million; while R_g is equal to the “residual gas” in the same original sample. R_g is defined by yet another formula:

$$R_g = 100 - 4.774(O_2) - CH_4 - C_2H_6 \tag{12}$$

In both of the above equations, the individual gases are expressed as percentages; except for CO, which is expressed as parts per million. Apparently Litton preferred to mix units for the different gases in order to keep the gas measurements in the units as they are commonly reported, although he does not state that.

Litton then used gas measurements that were taken from both laboratory experiments and from sealed areas of coal mines (in which there was “known” to be no fire) to calculate, for each sample, the R_I and another ratio – a residual gas-oxygen ratio (R_g/O_2). Litton does not explain why he uses the residual gas-oxygen ratio. He performed these calculations for approximately 155 samples, and then plotted these data points on a log/log graph of R-Index versus Residual Gas – Oxygen Ratio. His graph is reproduced here as Figure 3

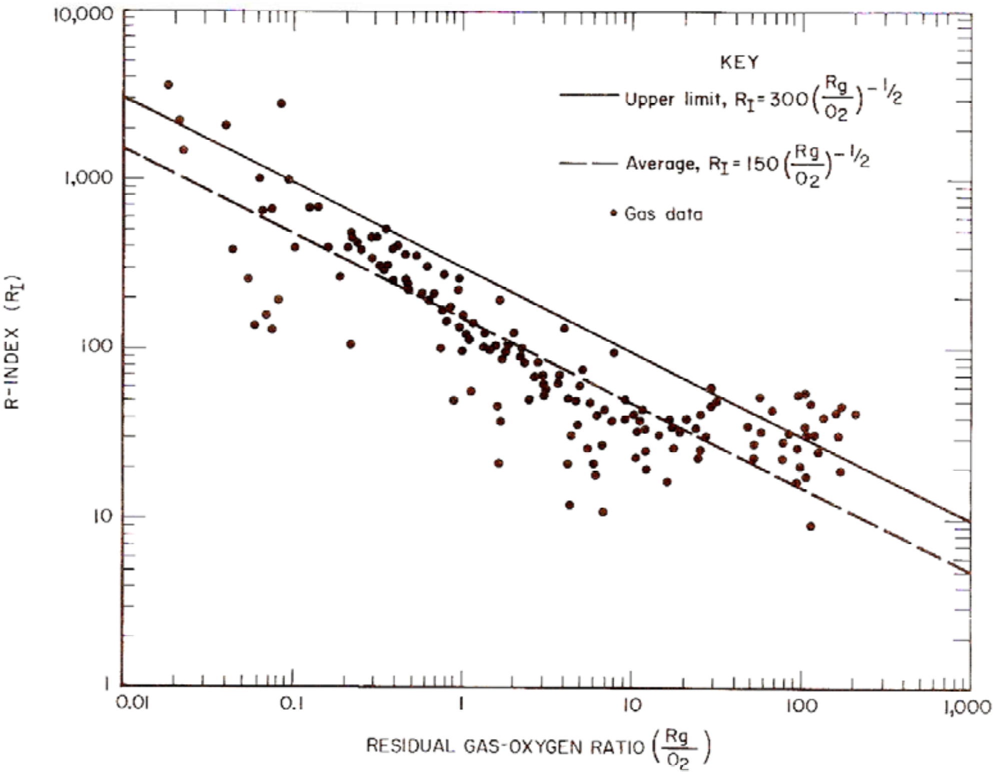

Figure 3
Litton's Graph of R-Index vs Residual Gas-Oxygen Ratio
The upper, solid line defines the limit for transition to ambient equilibrium.
The lower, dashed line is the "average" of all the data.
(Litton, 1986, p.5, Figure 1)

Litton then created two lines on this graph: a dashed line that he identified as the "average" for all the data; and a solid line that he identified as representing "the limit for transition to ambient equilibrium." Presumably "average" refers to a root mean square calculation. A methodology for generation of the solid line, "ambient equilibrium," is not provided. Litton does mention that the data points on the right side of the graph that are higher than his "ambient equilibrium" line are some of the data from lignite and sub-bituminous coal, whereas the data points above the ambient equilibrium line on the left side of the graph "are from samples of bleeder air taken adjacent to gob areas in an actual mine." He attributes these “outliers” to uncertainties in the oxygen measurements or the carbon monoxide measurements for the data points. (Litton, 1986, p.5)

The final step in this process, for any mine gas measurements, is to calculate the residual gas – oxygen ratio; and to determine from the ambient equilibrium line on the graph what the corresponding R-Index would be for ambient equilibrium. This ambient equilibrium R-Index is designated as “$(R_I)_{eq}$.” For any particular mine gas measurement, the actual R-Index is determined, and it is designated as “$(R_I)_{act}$ ” Finally, RATIO is determined as:

$$\mathrm{RATIO} = \frac{(R_I)_{act}}{(R_I)_{eq}} \tag{13}$$

Litton makes the point that any RATIO greater than 1 means that the mine atmosphere has not achieved ambient equilibrium, and therefore is not safe to reopen; whereas any RATIO less than 1 means that ambient equilibrium has been achieved, provided that RATIO is no longer declining but has stabilized. Litton then offers a number of historical examples for which the use of this RATIO would have indicated safe or unsafe conditions for reopening of an area of a coal mine that was sealed to extinguish a fire. Litton also cautions that in cases where the oxygen concentration is less than 1, a different Ratio (which he provides) must be used. He notes that this situation most frequently arises in gassy mines where methane liberation dilutes all other gasses to very low levels. (Litton, 1986, pp. 6-7)

Banerjee notes that Litton’s RATIO has some of the same limitations as other fire indices. Carbon monoxide readings can be misleadingly low due to bacteria; and very high methane or very low oxygen concentrations will create false readings. (Banerjee, 2000, p. 168)

2.3.2.3.10 Morris Ratio

Morris, in a 1988 article in *The Mining Engineer* titled "A New Fire Ratio for Determining Conditions in Sealed Areas," reviewed a number of observations and ratios that earlier researchers had proposed for monitoring underground coal mine fires. He uses data from some mine fires of the 1970's and 1980's to test previous work on Graham's ratio and the ratio of CO_2/CO; as well as a ratio $N_2/(CO+ CO_2)$, apparently developed by J.R. Partington in 1919 (whom Morris cites).

Morris concludes that Graham's Ratio does indeed increase with increasing temperatures, and that the CO_2/CO ratio declines at first and then levels off with increasing temperatures. As such, both these ratios are potentially useful for determining the state of a mine fire. He concludes that the best ratio though is the $N_2/(CO+ CO_2)$ ratio; which, he states, clearly indicates when a fire is active or passive, and which is very sensitive to a change in the state of the gases in a sealed fire zone. (Morris, 1988, pp. 374-375) Morris does not explicitly state it, but the gas concentrations in percent that are used in the ratio are apparently on a "firedamp and air free basis." This fact is surmised based on his use, for some of his calculations, of data in a table that is labeled as such. (Morris, 1988, p. 370, Table 2)

Morris does not address the possibility that carbon monoxide and carbon dioxide concentrations may experience extraneous gains or losses, as described in previous sections.

2.3.2.3.11 Carbon Monoxide Trend

For certain accessible areas of a coal mine, monitoring the concentration of carbon monoxide in a ventilated entry is now the regulatory standard. Any indication that the carbon monoxide level has exceeded a predetermined background must be investigated. (Office of the Federal Register, 2012)

However, for inaccessible areas, simply monitoring carbon monoxide levels is not satisfactory. Don Mitchell, in his book "Mine Fires," notes that miners usually become aware of the development of spontaneous combustion by finding unusually high concentrations of CO; and by that time, the spontaneous combustion has usually gone beyond the point of being easily controlled (Mitchell, 1996, p. 29). He states that CO monitoring systems are commonly used for fire detection, but their adequacy, even during the later stages of spontaneous combustion is limited. Mitchell attributes this inadequacy to two factors:

1. Limited pre-knowledge as to where spontaneous combustion may occur, and therefore where monitoring should take place;
2. The necessity of having no dilution of the air flow carrying any CO before the air flow reaches a detector (Mitchell, 1996, p. 30).

Of course, there can be other problems also, as already noted above. Carbon monoxide readings may indicate erroneously low levels due to low oxygen partial pressures, or adsorption on coal or soot, or dilution.

2.3.2.4 Indices of Explosibility

Another category of indices involves determining if a mine atmosphere, such as that in a sealed area, is potentially explosive or could become explosive with the introduction of air. Some of the earliest work in this area was published by H. F. Coward between 1928 and 1952, culminating in a United States Bureau of Mines Bulletin detailing a graphic called "Coward's Triangle." (Coward & Jones, 1952) The concept of a graphic for determining explosive, or potentially explosive, mine gas mixtures was expanded upon by M. G. Zabetakis, et al. in a 1959 Bureau of Mines Information Circular Number 7901. C. W. Ellicott introduced a simplified diagram in 1981.

Unlike the Jones – Trickett Ratio discussed above, these methods of determining explosibility do not seem to have found any use in the determination of concealed fires. No such mention was found in the literature; therefore, they were not pursued further.

2.4 Conclusions

Concealed coal mine fires, due to spontaneous combustion and ignitions, have been a problem for over a century. For more than a century, various gas measurements, and ratios of gas measurements, have been proposed as methods for detecting or monitoring concealed coal mine fires. All of the proposed measurements and ratios have significant limitations that always create a measure of doubt as to whether or not their use is yielding correct information. With the exception of the production of hydrogen and hydrocarbons, which has been shown to yield very late indications, any gas measurement that purports to give a measurement of a coal fire will have to measure combustion products. For coal fires, this means measuring in some way the consumption of oxygen and/or the production of carbon monoxide and/or carbon dioxide. However, there are significant problems with the measurements of all of these gases:

1. Oxygen concentrations can decrease, due to ambient temperature oxidation of coal and timbers, but still yield no fire. Blackdamp produced by this process can migrate out of inaccessible areas, especially due to barometric pressure changes, yielding oxygen readings that can be falsely interpreted. Oxygen consumption is typically interpreted, in some of the developed ratios, based on the assumption that nitrogen concentrations are the same in the air that is exiting an inaccessible area as it was in the

air that entered the inaccessible area. Again, blackdamp migration can render that assumption incorrect. Also, nitrogen gas can be desorbed by some coal seams. Oxygen concentrations from a fire scene may be diluted by other sources of fresh air that are introduced into the air stream before the fire air can be sampled.

2. Carbon dioxide concentrations can be diluted by fresh air flows or leakages before a sampling point, or such concentrations may be falsely reduced by dissolution of carbon dioxide in water. Carbon dioxide can be generated by the reaction of acid waters with carbonates. Carbon dioxide is desorbed in considerable quantities from some coal seams, and can be a significant and variable component of blackdamp.
3. Carbon monoxide concentrations, like the other fire gases, can be diluted by fresh air sources before the sampling point is reached. Carbon monoxide can be generated, sometimes in considerable quantities, by the low-temperature oxidation of coal, with no fire. Carbon monoxide can be adsorbed or absorbed by coal or soot or bacteria.

Given that all coal mine fire indices that can be applied to concealed fires have to rely on measurements of various combinations of oxygen, carbon monoxide, and carbon dioxide; and given that measurements of any of these gases may involve sources of error, a different approach is necessary if a definitive test for a concealed fire in an inaccessible area of a coal mine is to be developed.

Chapter 3: Radiocarbon as an Indicator of Concealed Mine Fires

A more definitive test for a concealed coal mine fire could involve monitoring for the existence of radiocarbon – carbon-fourteen (^{14}C) – in the carbon monoxide (CO) that is exiting an inaccessible area of a mine, such as a gob. This method will be referred to as "^{14}C-in-CO." CO is produced in coal mines at ambient temperatures, as a result of the oxidation of the freshly exposed coal. The CO produced from coal will not have any ^{14}C in it, due to the age of the coal, and the relatively short half-life of ^{14}C. However, the CO_2 that is constantly being drawn into a coal mine with the ventilating air flow will have the current level of ^{14}C in it. Under fire conditions – high temperatures – CO_2 can become CO, and then that CO will have ^{14}C in it. The details of this method are discussed below.

3.1 Some Basic Chemistry of Carbon-Fourteen

^{14}C is continually produced in the earth's upper atmosphere by the interaction of cosmic rays with nitrogen. Specifically, ^{14}C and a proton (*p*) are produced in a nuclear reaction between a neutron (*n*), produced by cosmic radiation, and a nitrogen atom; according to the reaction:

$$n + {}^{14}N \rightarrow {}^{14}C + p$$

The ^{14}C atoms, that are produced, react rapidly with oxygen in the upper atmosphere to produce CO_2, which permeates throughout the atmosphere and is absorbed by living plants and animals. As long as the plants or animals are alive, they are in an equilibrium with the ^{14}C that is in the atmosphere. However, when a plant or animal dies, it no longer takes in ^{14}C; and the amount of ^{14}C in the body of the plant or animals undergoes a steady decline due to radioactivity. This continual decline upon the death of a plant or animal allows for carbon-dating of such organic matter.

^{14}C radioactively decays to produce a nitrogen atom, an electron (*e*), and an electron antineutrino (*μ*); according to the reaction:

$$^{14}C \rightarrow {}^{14}N + e + \mu$$

^{14}C has a half life of approximately 5,730 years; which means that every 5,730 years, one half of an amount of ^{14}C will decay to ^{14}N. (Murnick et al, 2008) Reasonably accurate carbon-dating can be done for as long ago as 10 half-lives, or about 60,000 years. Simply detecting ^{14}C, without the need for accurate dating, can be done with even smaller amounts than would be available after 10 half-lives. After 10 half-lives, there would be about 1/1000 of the original amount of ^{14}C. ($2^{10} = 1054$) There are approximately 1.5 atoms of ^{14}C for every trillion atoms of ^{12}C present on earth, due to the continual production of ^{14}C in the upper atmosphere. After 10 half-lives of decay without replenishment, there would be approximately 1.5 ^{14}C atoms for every quadrillion atoms of ^{12}C. In a coal seam, which typically is on the order of one hundred million years old, there would be a negligible amount of the original ^{14}C remaining in the coal. There are some notable exceptions. A few, rare coal seams have very small, but measurable, amounts of ^{14}C in the coal. The amount of ^{14}C in these coal seams is on the order of 1/250 to 1/500 of the modern amount of ^{14}C. The ^{14}C has been attributed to the existence of uranium in the rock layers that are adjacent to the coal seam. (Hunt, 2002) A ^{14}C based test for fire could not be used in this type of coal seam.

3.2 The Boudouard Reaction

The Boudouard Reaction, also referred to as the Boudouard Disproportionation Reaction, or the Boudouard Equilibrium, is a reaction that involves CO, CO_2, and carbon (C). This reaction is expressed by the equation:

$$2CO \leftrightarrow CO_2 + C$$

This equilibrium was studied in 1905 by Boudouard. The reaction occurs at a very slow rate below 400°C. At elevated temperatures – above 400°C – a chemical equilibrium is established in a C/CO/CO_2 system. Above 700°C, the reaction strongly favors the production of CO. Any CO_2 in the atmosphere in a fire would be converted to CO. (Holleman and Wilberg, 2001)

CO is produced, in coal mines, by the low temperature oxidation of coal. In almost all coal mines, the only carbon that will have the modern amount of ^{14}C in it will be the CO_2 that is in the air that is drawn into the mine by the ventilating air currents. In accordance with the Boudouard Reaction, an interchange can take place that converts CO_2 to CO, but only at temperatures high enough to be associated with fire. If this interchange takes place, then the CO produced would have ^{14}C in it. In general, at any particular coal mine, the existence of ^{14}C in CO in a ventilating air stream would definitely indicate that there is a fire.

In order for the presence of ^{14}C in CO to be an indicator of fire, some method for testing for ^{14}C must be available. This method must be very sensitive, and must not suffer from interferences. The primary interference would be from the CO_2 in air, because CO_2 will always have ^{14}C in it. Any contamination with CO_2 would give a false positive. CO_2 will have to be removed before the test for ^{14}C, or the test for ^{14}C would have to be specific for ^{14}CO.

3.3 Methods of Testing for Carbon-Fourteen

Potentially, there are three different methods for testing for the existence of ^{14}C in CO. Two of the methods involve detecting the different mass of a ^{14}C atom versus a ^{12}C atom in the CO molecule, while the other method involves detecting the radioactive decay of the ^{14}C. The mass difference between ^{14}C and ^{12}C might be detected by accelerator mass spectrometry, or by laser spectroscopy. The radioactivity of ^{14}C might be detected with a liquid scintillation counter.

3.3.1 Accelerator Mass Spectrometry

The method for detecting ^{14}C that uses an accelerator mass spectrometer involves detailed sample preparation, and is only available at a limited number of research institutions. An accelerator mass spectrometer is essentially a very high velocity, high energy version of a regular mass spectrometer. Ions of atoms, to be analyzed, are subjected to high acceleration that allows separation not only of atoms that have the same number of protons – but differ by the number of neutrons – such as ^{14}C and ^{12}C, but also allows for the separation of atoms that have the same total number of protons and neutrons – but have that same number with different individual numbers of protons and neutrons, such as ^{14}C (6 protons and 8 neutrons) and ^{14}N (7 protons and 7 neutrons). (Davis, 2014) Gas samples could be sent to one of the institutions that have an accelerator mass spectrometer, for testing; but such gas samples could not have any modern CO_2 in them, because the modern CO_2 would yield a false positive. A chemical process would have to be used first to remove any trace of CO_2. Overall, this approach was judged to be too expensive for proof-of-concept tests, and too inconvenient for practical field use.

3.3.2 Laser Spectroscopy

The detection method involving laser spectroscopy is based on the ability of lasers spectrographs to distinguish between CO molecules that have ^{14}C in them (^{14}CO) and CO molecules that have ^{12}C in them (^{12}CO) – by detecting the different molecular bond vibration frequencies due to the different masses of the carbon atoms in the molecules. This technique would have the advantage of not requiring a step to separate out CO_2 before testing for ^{14}CO. The carbon-oxygen bonds in CO_2 will vibrate at a different frequency than the carbon-oxygen bonds in CO, and these different frequencies can be isolated by a laser spectrometer. Another advantage in this technique, if sensitive lasers become widely available, is that monitoring of CO for the presence of ^{14}CO could take place continuously at a mine. However, such laser spectrometers are not widely available at present.

The most sensitive laser spectrometers have been developed at a few research institutions for the detection of ^{14}C in CO_2. These lasers are specifically designed to study CO_2, and would not be applicable for CO. Apparently, no work is currently being done that involves extremely sensitive laser spectrometers that are specific to CO. Some idea of the potential for this method can be gotten from the literature. In an article titled "Intracavity Optogalvanic Spectroscopy, an Analytic Technique for ^{14}C Analysis with Subattomole Sensitivity," the authors state that they were able to achieve limits of detection near 10^{-15} ^{14}C/^{12}C ratios, and that such detection limits are comparable to those achieved by accelerator mass spectrometers. (Murnick, et al, 2008) Some indication of the hope for the future of this technique is contained in a paper by Labrie and Reid. They report achieving a limit of detection for ^{14}C in CO_2 of 10^{-12} using a tunable diode laser and a short multi-pass optical cell. Tunable lasers are available for use with CO. The authors claim they should be able to achieve an order of magnitude better of the limit of detection by using a longer multi-pass cell. While a limit of detection of 10^{-13} is still not good enough for use in the anticipated coal mine fire scenario, it is getting close. (Labrie & Reid, 1981)

Unfortunately, laser spectroscopy is still under development; and is not yet available, except in a few research laboratories. Developing a laser spectrometer of suitable sensitivity for CO was also judged to be too expensive for this proof of concept work.

3.3.3 Liquid Scintillation

Liquid scintillation is a method for detecting low energy alpha and beta particles. A substance that contains a low energy beta emitter, such as ^{14}C, is dissolved in a special mixture of chemicals. The mixture of chemicals will emit photons when a beta particle is emitted by a decaying ^{14}C atom. The photons are detected, and counted, by sensitive photomultiplier tubes, in an instrument known as a liquid scintillation counter.

Based on widespread availability and long history of use, liquid scintillation counting was chosen as the method for the detection of ^{14}CO for this study. A literature search was conducted in order to determine possible methods for capturing CO for testing for the presence of ^{14}CO. Several possible physical and chemical methods were identified for collecting CO for testing, while not simultaneously collecting CO_2.

3.3.3.1 Sample Preparation for Liquid Scintillation

Liquid scintillation, based on detecting the radioactivity of ^{14}C in CO, would involve collecting CO from a mine atmosphere without collecting CO_2. The collection of the CO would have to be done in a fluid that could then be tested in a liquid scintillation counter for the decay of the ^{14}C. Potentially, the CO could be collected in a single step; or the CO could be collected in a second step after CO_2 is collected in a preliminary step. Several potential problems are anticipated:

1. The concentration of CO in mine atmospheres will be very low.
2. Collection times may be very long, resulting in loss of volatile fluids, including water.
3. Even if a fluid is very specific for the absorption of CO, long collection times may result in some absorption of CO_2,
4. Mine atmospheres may have contaminants that will interfere with the collection of CO.

The collection of CO would have to be accomplished with the concentration of CO from a mine atmosphere in which the CO is present at the parts-per-million level. Concentration will likely be difficult to impossible. Concentration of a gas in a liquid is dependent on the partial pressure of the gas. The partial pressure of the CO will be very small – on the order of magnitude of 1 to 10 millionths of an atmosphere of pressure. Any liquid that might capture CO at these very low partial pressures would have to have a very strong affinity for CO.

From the literature, several different methods were identified that might allow for the separation of CO and CO_2, and the ultimate testing for CO with a liquid scintillation counter. The various methods considered were:

1. Cryogenic separation of CO and CO_2
2. Absorption of CO by nickel (Ni)
3. Absorption of CO by a toluene solution of copper chloride ($CuCl_2$) and aluminum chloride ($AlCl_3$)

4. Absorption of CO by an aqueous solution of $CuCl_2$ and magnesium chloride ($MgCl_2$)
5. Absorption of CO_2 by an aqueous solution of potassium hydroxide (KOH)
6. Absorption of CO_2 by Carbo-sorb®

Cryogenic separation of CO and CO_2 would rely on flowing mine gases through a collection trap cooled with liquid O_2. CO_2 has a sublimation temperature of minus 78.5°C at atmospheric pressure, whereas CO liquefies at minus 191.5°C. Liquid O_2 has a boiling point of minus 183°C, and could be used to freeze the CO_2 in the trap, but would let the CO pass through for later collection. The later collection of CO could be accomplished with a second cold trap chilled with liquid N_2, which has a boiling point of minus 196°C; or by some other means. If CO were trapped with liquid nitrogen, it would still have to be transferred to a liquid in yet another step, for testing in a liquid scintillation counter. Another possible concern is the possibility that a very small amount of CO_2 will make it through the CO_2 trap – contaminating the CO. Cryogenic separation would not be impossible to implement in the field, but it could be expected to be difficult. There would also be safety concerns with the handling of super-cold materials.

CO reacts strongly with Ni to form nickel carbonyl – $Ni(CO)_4$. Nickel carbonyl is a liquid that forms at room temperature. CO_2 does not react with Ni, so this method might be ideal for separating the two gases. Unfortunately, nickel carbonyl is a probable carcinogen, a poison inhalation hazard, and is flammable and reactive. Very strict safety measures would have to be followed when working with this compound, and its use under field conditions would be problematic. (McGraw-Hill, 1982, b)

CO is readily absorbed, at room temperatures, by a solution of $CuCl_2$ and $AlCl_3$ in toluene. Descriptions of the process are oriented toward industrial scale purification of CO; therefore, information available in the literature does not include absorption of CO at very low partial pressures. However, the absorption is reversible by varying the temperature and CO pressure, indicating that the complex that is formed is not very strong. Unfortunately, the solution is black, and therefore would not be amenable to liquid scintillation counting. (Hogendoorn, et al, 1995)

CO can be absorbed in an aqueous solutions of $CuCl_2$ – and aqueous solutions of $CuCl_2$ and other chloride salts, such as magnesium chloride ($MgCl_2$). (Katsumoto, et al, 1988) These solutions will not be black, but they will be blue-green. Again, these chemical systems for the absorption of CO have been studied in order to find a better system for CO purification on an industrial scale. Data generally indicate that these various copper based aqueous solutions may be able to concentrate CO from parts-per-million concentrations in the atmosphere of a coal mine, but that is not a certainty. CO_2 absorption may also be a problem, although CO_2 absorption may be slight, due to these solutions being very acidic.

CO_2 could be absorbed by an aqueous solution of KOH or NaOH. This fact might be used to eliminate CO_2 from a gas stream before trying to absorb CO with another chemical, if there was a possibility of the CO_2 interfering with the CO absorption. If there were a concern about CO_2 interfering with a subsequent absorption step for CO, CO_2 might also be absorbed first in Carbosorb®, a proprietary chemical specifically designed for absorbing CO_2 for testing in a liquid scintillation counter. Unfortunately, there does not appear to be any studies that report the efficiency of the hydroxides, or Carbosorb®, in absorbing CO_2. If the absorption of CO_2 is not very close to 100%, the small amount of CO_2 that escapes capture would contaminate the CO. Also complicating matters: there is no information readily available concerning the absorption of CO by these CO_2 capturing solutions. Because CO would be present in very small amounts in any mine atmosphere undergoing absorption, any absorption of CO in a CO_2 capture step would be a serious loss. Also, all the chemicals are very strong bases. Use in the field would have to be done with care.

3.4 Initial Experiments to Capture CO_2

Because of all the concerns, expressed above, involving all the different, potential, separation and capture methods; initial trials were conducted for what was thought to be one of the more straight-forward and safer capture procedures – the capture of CO_2 in Carbosorb®. The captured CO_2 was then analyzed by a liquid scintillation counter to see how well a liquid scintillation counter might work for the anticipated levels of ^{14}C. The experimental set-up for capturing CO_2 from air is illustrated in Figure 4. Air, which was sucked through the components of the experimental set-up by a vacuum pump, was first drawn through a flow meter. Then the air was drawn through an aspirator tube that was submerged in Carbosorb® in a tall cylinder. From the tall cylinder, the air entered an Erlenmeyer flask, that was installed in the flow path to keep any Carbosorb® from being sucked into the vacuum pump.

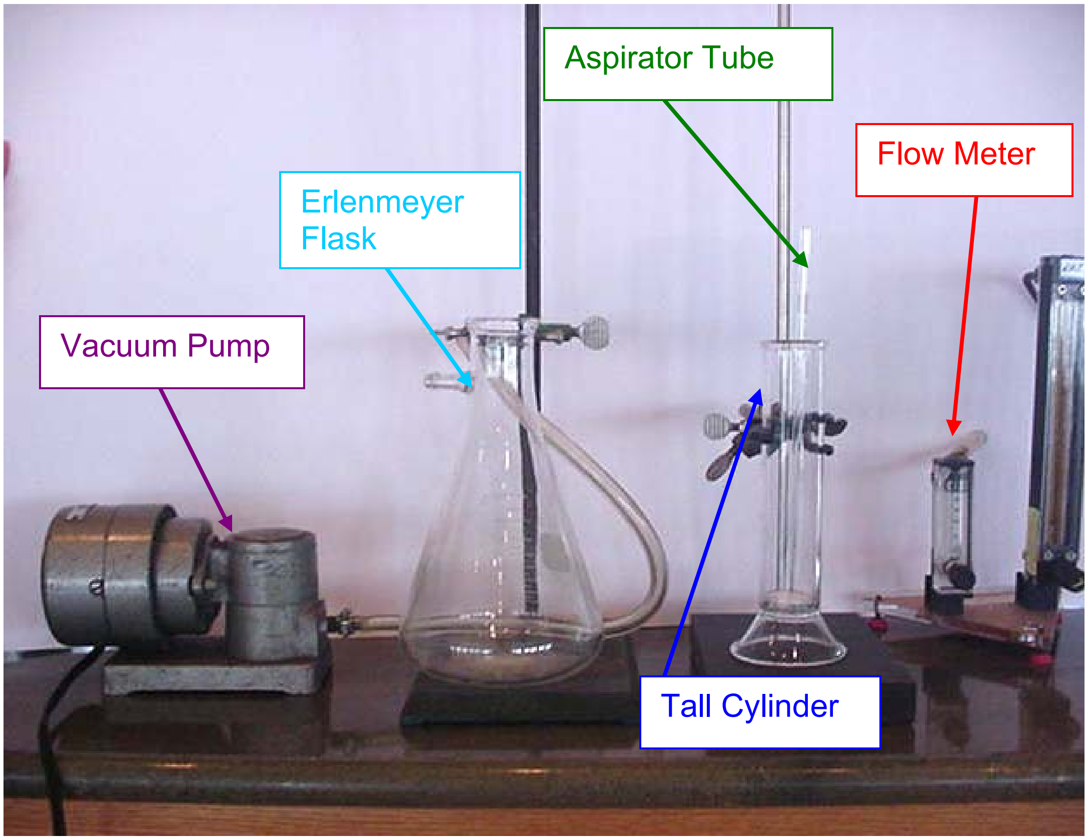

Figure 4

Experimental Apparatus for Capturing CO_2 from Air

With the experimental apparatus above, air would be drawn through the Carbosorb® for periods of 30, 60, and 120 minutes in an effort to saturate the Carbosorb® with CO_2. A sample of the fluid from the tall cylinder would then be put in a 20 milliliter vial for analysis in a liquid scintillation counter.

Qureshi, et al. reported that Carbosorb® has a practical absorption capacity of about 6 millimoles of CO_2 per milliliter. (Qureshi, et al., 1989, p. 626) The radioactivity of ^{14}C is approximately 14 disintegrations per minute per gram of pure, modern carbon. (McGraw-Hill, 1982) A 20 milliliter vial should have as much as 120 millimoles of CO_2, if the fluid is saturated with CO_2. A mole of carbon weighs 12 grams, therefore, 120 millimoles of CO_2 would have 1440 milligrams of carbon – or 1.44 grams. This amount of carbon would have about 20 disintegrations per minute. Each disintegration will produce a beta particle with an average energy of 49 kilo-electron-volts (kev). Approximately ten photons are produced per kev, therefore, 20 disintegrations x 49 kev x 10 ~ 9,800 photons per minute. (L'Annunziata, 2012)

Unfortunately, when all the vials for all the different times were analyzed, all the vials had about the same level of activity, and they were all too low (~ 300 to 400 photons/minute) compared to expectations based on the above calculation. Severe quenching due to water was the most likely cause – a problem that would likely be worse with mine gas samples. Worse, the Carbosorb® had a very high rate of evaporation, which prohibited long run times. For the 60 minute and 120 minute runs, the Carbosorb® in the tall cylinder had to be replenished, which had a diluting effect.

Given all the potential problems with all the potential processes for separating CO and CO_2, and capturing the CO; especially the safety concerns and the low CO partial pressure concerns, a different approach was pursued, as explained in the next chapter.

Chapter 4: Selection of a Fire Indicator Gas

Given the problems noted in Chapter 3, and the numerous extenuating circumstances associated with the use of the different product-of-combustion gases and the different ratios of such gases discussed in Chapter 2, along with the attendant lack of certainty with their use; a different approach for determining whether or not there is a concealed fire in a coal mine was sought. One approach, that seemed to offer hope of a more definitive indication of fire, would be to introduce a select gas into the inaccessible area that would yield a distinctive decomposition product if it came into contact with fire temperatures. Gas samples, recovered from an exit of the inaccessible area, could be tested for the decomposition product. This is a novel concept. A proposed gas that would yield distinctive decomposition products in a fire area will be referred to as a Fire Indicator Gas (FIG).

An ideal fire indicator gas would have the following properties:

1. Be a gas at ambient mine temperatures.
2. Be non-toxic.
3. Be nonflammable, non-corrosive, etc.
4. Yield a distinctive combustion (decomposition) product that is a gas at ambient temperatures, and is non-toxic.
5. Combustion/decomposition must take place in the temperature range of burning coal.
6. The gas of both the fire indicator gas and the combustion product should be readily detectable by some means when the gases are present in relatively small amounts.
7. The fire indicator gas should be readily available, and reasonably priced.
8. The gas of both the fire indicator gas and the combustion product should have a specific gravity as close to that of air as possible.

9. Both the initial fire indicator gas and the combustion product gas should not be too soluble in water.

Although a fire indicator gas might not have to have all of these ideal properties, initial screening of possible candidates was conducted based on this list.

A quick review of the periodic chart narrows the choices as to where to look for possible candidates:

1. All of the metals on the left-hand side of the periodic chart are ruled out. Some metals do have volatile compounds, such as chlorides, but any metal, upon combustion, can be expected to yield a metal oxide. No metal oxides are gases at ambient temperatures. Furthermore, volatile metal chlorides (and other halides) are toxic and very water soluble.
2. The non-metals of primary interest will be the elements occupying the right-hand side of the first row: B, C, N, O, and F; and the right-hand side of the second row: Si, P, S, and Cl. The second row elements will form heavier compounds.
3. Compounds of the non-metals of the third and fourth row: As, Se, and Br; and Sb, Te, and I, are likely to be too toxic and/or form gases that have too high a specific gravity.
4. In the right-hand side of the first and second row, B, Si, and P can almost certainly be ruled out. The oxides of all three elements are solids at ambient temperatures. The only volatile compounds of B, Si, and P are the hydrides and halides. The hydrogen compounds of B are pyromorphic, and the hydrogen compounds of Si and P are extremely toxic. The halides of all three elements are extremely toxic.

The above eliminations leave compounds of H, C, N, O, F, S, and Cl for further consideration.

1. Generally, the C, N, and S in any gaseous compounds will tend to form oxides when broken down completely by heat, while the F and Cl will tend to form hydrides (HF and HCl). These simple oxides and hydrides, that are the result of heat, cannot themselves be used as a fire indicator because all these oxides and hydrides will be very water soluble.
2. Apparently, some simple organic molecule must be used. A relatively complex molecule will be relatively heavy (dense).
3. Some organic compounds may not break down completely to the end products of simple oxides or hydrides, especially if the compound is not exposed to a great amount of heat for a long time.

Therefore, the fire indicator gas must be some relatively simple organic molecule that contains one or more N, S, F, and/or Cl atoms; and that will yield some partial decomposition product that is distinctive.

One class of compounds that offer some possibilities with respect to partial decomposition are chlorofluorocarbons, such as halons and refrigerants. There is a body of fairly recent literature on the combustion of various fluorocarbons and chlorofluorocarbons due to recent research into substitutes for the traditional halons that have been found to be ozone depleting chemicals. The main goal of this research seems to have been to determine the maximum amount of hydrofluoric acid and carbonyl fluoride that can be produced by these substitutes when they were used to extinguish a fire, so the papers did not study partial combustion products (e.g. Dupont, 2013). However, a few papers have been published that offer some insight into the possibility of halon and refrigerant chemicals only partially decomposing under some circumstances. In an article titled “Experimental and Computational Studies of the Thermal Decomposition of Halon 1211,” by Yu, et al. (2005), numerous partial reactions are noted that could yield novel combustion products, although their work was done in a non-oxygen atmosphere. Halon 1211 is the compound $CBrClF_2$ – a relatively simple halogenated organic molecule, and yet under pyrolysis it yielded a number of other compounds. Quoting Yu et al:

> “Thermal pyrolysis of halon 1211 ($CBrClF_2$), diluted in nitrogen, in a tubular alumina reactor, has been studied over the temperature range of 773–1073 K at residence times from 0.3 to 2 s. At temperatures below 973 K, the major products were CCl_2F_2, CBr_2F_2, $C_2Cl_2F_4$, C_2BrClF_4, C_2F_4, and $C_2Br_2F_4$. Further increasing temperature resulted in the formation of $CBrF_3$, $CClF_3$, and many other species whose formation necessitated the rupture of $C—F$ bonds.” (Yu et al, 2005, p. 134)

Reacting Halon 1211 in an oxygen rich environment would yield different products than were created in the nitrogen environment, but there is still the possibility of such a reaction yielding some products that would be definitive of fire, if there is incomplete combustion.

An early article, on the use of gas chromatography to separate various low molecular weight fluorocarbons, by Bright and Matula, offers particular insight into the possibility of this class of compounds serving as a fire indicator gas. These authors mention a certain combination of gas chromatograph columns and operating conditions that allowed them to separate “the major equilibrium products associated with fluorocarbon combustion,” which included oxygen (O_2), tetrafluoromethane (carbon tetrafluoride, CF_4), carbon dioxide (CO_2), carbonyl fluoride (CF_2O), and tetrafluoroethene (C_2F_4). (Bright & Matula, 1968, p. 222) Their chromatogram is reproduced here as Figure 5.

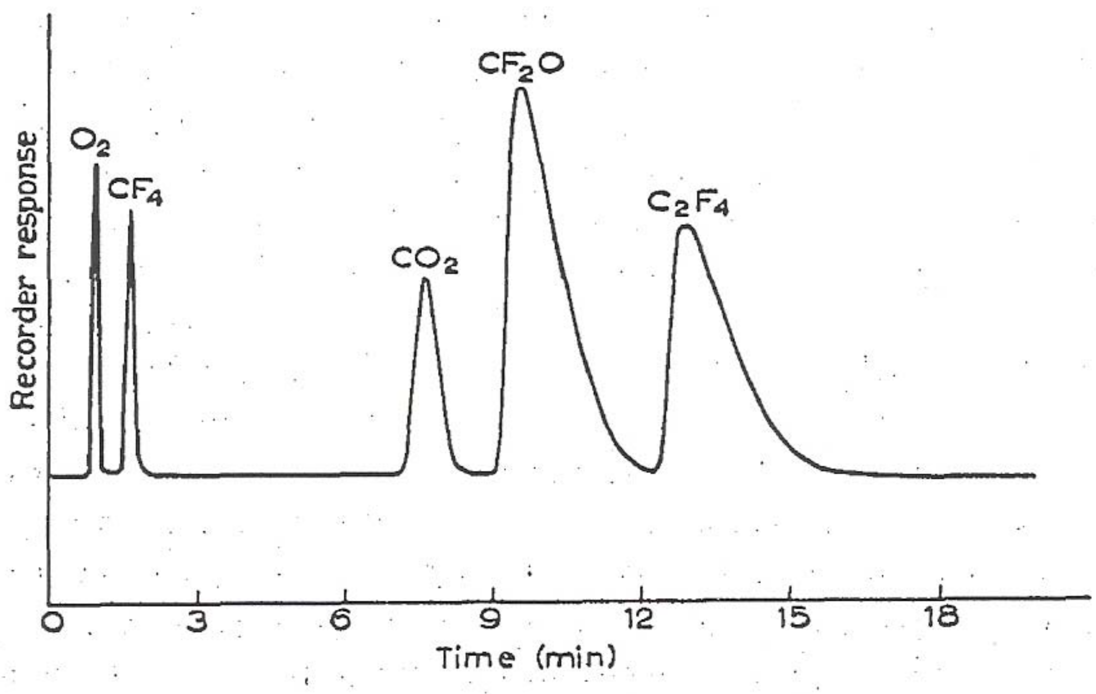

Figure 5
Typical Chromatogram of C_2F_4 Oxidation Products
From Bright and Matula (1968, p. 221, Figure 2)

The appearance in the chromatogram of a prominent tetrafluoromethane (CF_4) peak is especially encouraging. This compound is relatively stable, and could well be a significant fire product of any longer chain fluorocarbon, or any chlorofluorocarbon. It would likely serve as the primary indicator that any longer chain halogenated hydrocarbon gas had been broken down by the high temperatures of a fire.

All this raises the likelihood that halons, or other chlorofluorocarbons, could be used as a fire indicator gas that would yield novel fire products. Generally, these different halons will be relatively insoluble in water, as will be the decomposition products. However, the halons and their products will be relatively dense. The simplest, lightest fluorocarbon, CH_3F has a specific gravity for its gas of 1.195.

CH_3Cl has a specific gravity of 1.74. Every additional F or Cl atom will only increase the specific gravity.

One source of potential candidates for fire indicator gases is a publication of the United States Environmental Protection Agency (EPA) titled “Halon Substitutes Under SNAP.” (EPA, 2012) SNAP is an acronym for “Significant New Alternatives Policy,” the EPA’s program that evaluates alternatives to ozone depleting chemicals. Chemicals that are SNAP approved are the chemicals that will be used for fire-fighting chemicals in place of the previously used halons, that have been banned from future production due to their ozone depleting nature. These approved chemicals can be expected to be more readily available, and therefore less expensive, than other chemicals in the same class of compounds might be. Table 3 is a list of all the halogenated hydrocarbons that are approved under SNAP.

Table 3

All of the Currently SNAP Approved Halogenated Organic Compounds for Fire Extinguishants, with Boiling Points and Water Solubility.

Items in Red Are Less Favorable Because of Too High Boiling Point and/or Solubility.

Chemical	Boiling Point ºC	Solubility Water	Trade Names
1-Chloro-1,2,2,2-Tetrafluoroethane (Dupont, 2012a)	-12 ºC	1.45 g/L	HCFC-124 FE-241
2,2-Dichloro-1,1,1-Trifluoroethane (Dupont, 2012b)	**28 ºC**	**3.9 g/L**	HCFC-123 FE-232
1,1,1,2,3,3,3-Heptafluoropropane (Dupont, 2011a)	-16 ºC	Not Available	HFC-227ea FM-200
1,1,1,3,3,3-Hexafluoropropane (Dupont, 2010b)	-1 ºC	Not Available	HFC-236fa FE 36
CF_3I	-23 ºC	“insoluble”	
Octafluoropropane – C_3F_8 (Airgas, 2010)	-37 ºC	Not Available	Freon 218
C_4F_{10} (F2 Chemicals Ltd, 2011)	-2 ºC	“insoluble”	Not Available
n-C_6F_{16} (Top Fluorochem Co., 2009)	**57 ºC**	10 ppm	Not Available
C6-perfluoroketone (3M Company, 2007)	**49 ºC**	Nil	Novec 1230
CF_2Cl_2 (Dupont, 2011b)	-41 ºC	**2.6 g/L**	HCFC-22 R-22
CHF_3 Dupont, 2011c)	-82 ºC	1.0 g/L	HFC-23 FE13
1,1,1,2,2-Pentafluoroethane (Dupont, 2010a)	-48 ºC	0.09wt%	HFC-125 FE25
1,1,1,2-Tetrafluoroethane (Dupont, 2012c) Listed in earlier SNAP. Not in latest SNAP, but approved for automobile refrigerant	-26 ºC	0.15wt%	HFC-134a

From Table 3 of SNAP approved compounds, several compounds can be considered as less favorable candidates for use as a FIG. Three of them – 2,2-Dichloro-1,1,1-Trifluoroethane, n-C_6F_{16}, and C6-perfluoroketone – have boiling points above ambient temperature, although they all have significant volatility that still allows their use as fire extinguishants. Other compounds in the table have other properties that may be marginal. 2,2-dichloro-1,1,1-trifluoroethane and CF_2Cl_2 have solubilities in water that may be too high.

Ultimately, from Table 3, four different compounds were selected for initial testing based on the above screens – all various fluorocarbons:

1. Octafluoropropane – $CF_3CF_2CF_3$
2. 1,1,1,3,3,3-Hexafluoropropane – $CF_3CH_2CF_3$
3. 1,1,1,2-Tetrafluoroethane – CF_3CH_2F
4. C6-perfluoroketone – $CF_3CF_2C(=O)CF(CF_3)_2$

One additional compound was selected for trial that is a fluorocarbon, but is not a fire extinguishant, and therefore is not subject to the SNAP list above – 1,1-difluoroethane, which can be represented as CH_3CHF_2. 1,1-difluoroethane has a boiling point of -25 ºC, and a solubility in water of 0.28 weight% at 25º C. (Scientific Instrument Services, 2014) Some additional details on all five of these compounds are listed below.

Octafluoropropane was selected as the most viable of the totally fluorinated hydrocarbons (the other two being C_4F_{10} and n-C_6F_{16}) because of vapor density considerations. As shown in Table 4 below, the specific gravity of octafluoropropane is already high, at 6.68. The specific gravity of C_4F_{10} is 9.7, and the specific gravity of n-C_6F_{16} would be even higher. Based on basic chemistry, octafluoropropane should be more stable, and therefore more difficult to decompose, of any of the proposed FIGs. Samples for experimentation were obtained from Airgas.

1,1,1,3,3,3-Hexafluoropropane was selected over the other propane molecule on the SNAP list that is not totally fluorinated – 1,1,1,2,3,3,3-heptafluoropropane – because it should decompose more easily. It should also decompose more easily than octafluoropropane. Samples for experiments were obtained from an FE-36 fire extinguisher.

1,1,1,2-Tetrafluoroethane was chosen over the other ethane based molecule on the SNAP list that is not totally fluorinated – pentafluoroethane – because it is readily available, since it is used in modern automobile air conditioner systems (where it is known as R134a), and because it should decompose easier. Samples were obtained from a commercially available can of automobile air conditioner refrigerant.

C6-perfluoroketone is also known by the systematic name 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone. It was selected for trial because the carbon atom in the middle of the base pentane molecule that is double-bonded to the oxygen atom (indicated by the “C” in front of the (=O) in the formula: $CF_3CF_2C(=O)CF(CF_3)_2$) should be especially susceptible to attack by high temperatures, and ultimate decomposition into smaller molecules. Although C6-perfluoroketone is a fluid at ambient temperatures, it has a high vapor pressure and readily evaporates at ambient temperatures. Samples were obtained from a Novec 1230 fire extinguisher.

1,1-Difluoroethane was selected for experiments for both its ready accessibility and its probable ready decomposition when exposed to heat. This compound has been approved by the EPA for use as a new air conditioner refrigerant for automobiles (for which it is referred to as R152a), and is approved for use for pressurizing small containers of household goods. Samples for experiments were obtained from a can of “3M Dust-Remover” “canned air” cleaner – readily available in the electronics section of stores. This compound has the lowest ratio of fluorine atoms to hydrogen atoms of any of the fluorocarbons selected, with just 2 fluorine atoms – both on the same carbon atom. It should be the least stable to thermal decomposition of any of the proposed FIGs.

Some properties of these five FIGs, and other gases of interest, are summarized in Table 4.

Table 4
Critical Properties of the Selected, Potential Fire Indicator Gases, And Other Gases of Interest

Type of Gas	Compound	Formula	Specific Gravity	Boiling Point ºC
Possible FIG	Octafluoropropane	$CF_3CF_2CF_3$	6.68	-36.7
Possible FIG	1,1,1,3,3,3-Hexafluoropropane	$CF_3CH_2CF_3$	5.3	-1
Possible FIG	1,1,1,2-Tetrafluoroethane	CF_3CH_2F	3.25	-26
Possible FIG	C6-Perfluoroketone	$CF_3CF_2C(=O)\text{-}CF(CF_3)_2$	11.6	49
Possible FIG	1,1-Difluoroethane	CH_3CHF_2	2.4	-25
Standard Tracer Gas	Sulfur Hexafluoride	SF_6	5.11	-63.9
Common Mine Fire Gas	Carbon Monoxide	CO	0.97	-192
Common Mine Gas	Carbon Dioxide	CO_2	1.52	-79

Other fluorocarbons or chlorofluorocarbons could be selected for later experimentation based on results obtained from trials with these FIGs. All five of these initial gases have the potential to comply with all of the elements of the list of ideal properties except item #6 – specific gravity. The specific gravities of all the gases are significantly heavier than air; but they are all, except for octafluoropropane and C6-perfluoroketone, significantly lower than sulfur hexafluoride – which is a well documented tracer gas that has a long history of use in mine ventilation work. In addition, C6-perfluoroketone has a higher than ambient temperature boiling point.

Chapter 5: Experiments to Establish Fire Indicator Gases

Experiments were conducted to test the five different proposed FIGs in order to determine if any of the gases, if introduced into ventilating air-streams in a mine, could be used to test for the presence of fire in a mine. An indication of fire would be achieved based on the initial gas yielding novel, detectable, decomposition products when exposed to temperatures associated with a fire.

Based on basic chemical considerations, all five of the initial gases selected above have the potential, when exposed in air to temperatures associated with fire, to form various smaller molecules than the parent molecule that could then be detected using a gas chromatograph. For example, 1,1,1,3,3,3-hexafluoropropane may breakdown into products that have two carbon atoms, with various combinations of hydrogen and fluorine atoms attached, and/or one carbon atom, with various combinations of hydrogen and fluorine atoms.

5.1 Experimental Determination of Purity:

The first set of experiments consisted of checking the five proposed fire indicator gases for purity. Because very high purity gases are not being used, each gas has the potential to have various levels of contaminants. Determining the level and types of contaminants is important, in order to make sure that no potential decomposition products are already present in the original gas.

The chemical processes that are used to make the proposed FIGs do not involve the anticipated primary decomposition chemicals, such as carbon tetrafluoride, but could possibly involve some precursors to the primary decomposition chemicals. For example, the manufacture of 1,1,1,3,3,3-hexafluoropropane is accomplished by one of three processes (National Academy of Sciences, 1997, Chap 2, p14):

(1) $CCl_2{=}CClCCl_3 + HF \rightarrow CF_3CCl_2CF_3 + CF_3CHClCF_3$

$CF_3CCl_2CF_3 + CF_3CHClCF_3 + H_2 \rightarrow CF_3CH_2CF_3$

(2) $CCl_2{=}CCl_2 + CCl_4 \rightarrow CCl_3CH_2CCl_3$

$CCl_3CH_2CCl_3 + HF \rightarrow CF_3CH_2CF_3$

(3) $(CF_3)_2C{=}CF\text{-}O\text{-}CH_3 \rightarrow CF_3CH_2CF_3 + CO_2 + CH_3OH$

If the second process is used, one of the anticipated decomposition products could possibly be a contaminant in the FIG. If some of the carbon tetrachloride - CCl_4 - used in the first step of the second process is carried into the second step and fluorinated, some carbon tetrafluoride could be in the resultant 1,1,1,3,3,3-hexafluoropropane.

All five initial gases were checked for levels of impurities by injecting a 10 micro-liter (ul) sample of each gas into a Shimadzu GCMS-QP2010 Ultra gas chromatograph-mass spectrograph with an Agilent H-P Plot Q column. The column was 30 meters long, with a diameter of 0.320 millimeters and a film thickness of 20 micrometers. The carrier gas was helium, flowing at a linear velocity of 40 cm/sec; with a total flow of 14 mL/min, a column flow of 1.23 mL/min, and with a pressure of 31.5 kPa. A split ratio of 10:1 was used. The column temperature was programmed to run at 40º C for 3 minutes, and then increase in temperature at a rate of 30º C per minute up to 150º C, and hold that temperature for 10 minutes. The total temperature program run time was 16.67 minutes. The mass spectrometer start time was set at 1.95 minutes in order to avoid all but the tail of the air peak, but to catch any tetrafluoromethane, which peaked at 2.06 minutes with this protocol. The mass spectrometer was set to scan for 35 to 400 mass-to-charge ratio, at a scan speed of 2000. This protocol was used for all the analyses in this study.

The results of the tests of the five possible FIGs for contaminants are shown below. As can be seen in Figure 5, the octafluoropropane standard that was used for combustion/decomposition experiments has a small amount of 1,1,1,3,3,3-hexafluoropropane contamination. Therefore, if 1,1,1,3,3,3-hexafluoropropane should happen to be a combustion product, or decomposition product of octafluoropropane, it could not be used as an indicator of fire. Some other distinct gas product would also have to be created in order to unequivocally indicate fire temperatures.

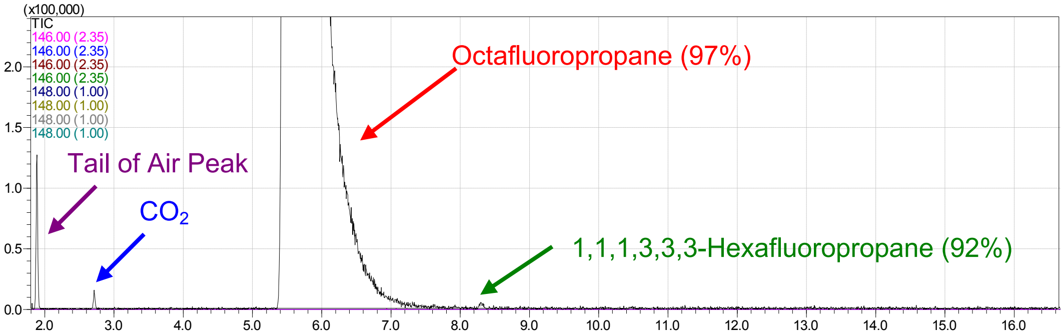

Figure 6
Gas Chromatogram of Octafluoropropane Standard
Mass Spectroscopy Identification of Peaks are Shown by Different Colored Arrows and Text, with the Percent of Confidence in the Identification by the Mass Spectrometer Given in Parenthesis

In the case of hexafluoropropane, Figure 6 indicates that there was no significant contamination of the standard. Presumably, any distinctive gaseous product generated by heating this standard could be used as an indication of fire.

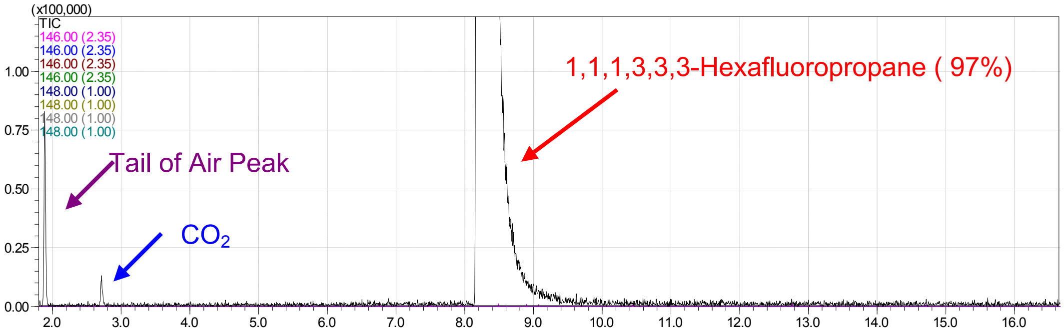

Figure 7

Gas Chromatogram of 1,1,1,3,3,3-Hexafluoropropane Standard

Mass Spectroscopy Identification of Peaks are Shown by Different Colored Arrows and Text, with the Percent of Confidence in the Identification Given in Parentheses.

Figure 7 indicates that the 1,1,1,2 tetrafluoroethane standard had a small amount of the contaminant 1,1,2,2 tetrafluoroethane. Therefore, that contaminant in the standard cannot be used to indicate fire.

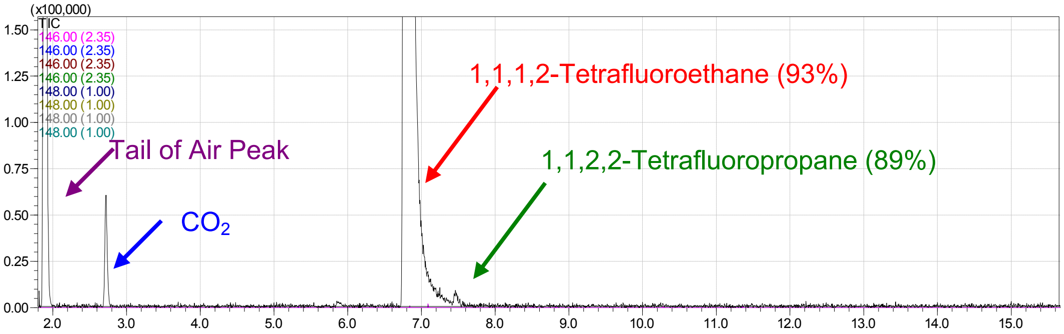

Figure 8

Gas Chromatogram of 1,1,1,2-Tetrafluoroethane Standard

Mass Spectroscopy Identification of Peaks are Shown by Different Colored Arrows and Text, with the Percent of Confidence in the Identification Given in Parenthesis.

The C6-perfluoroketone also had a contaminant of 1,1,1,3,3,3-hexafluoropropane; therefore, that contaminant cannot be used as a product of combustion or decomposition of C6-perfluoroketone.

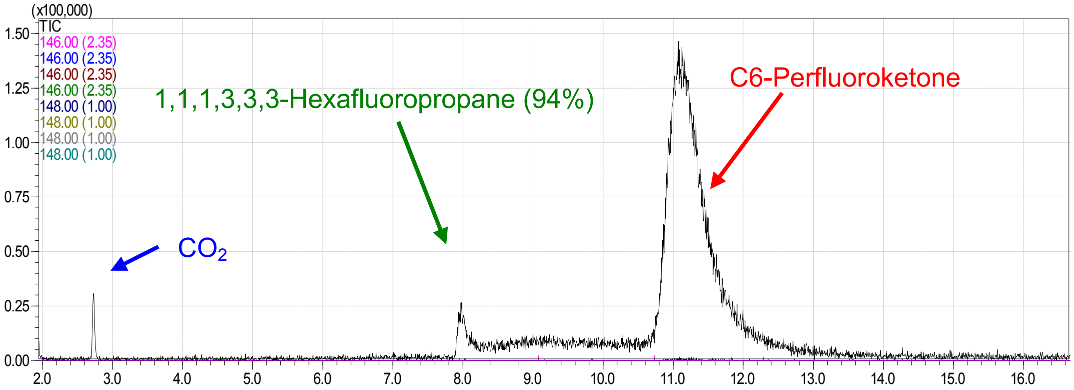

Figure 9

Gas Chromatogram of C6-Perfluoroketone Standard

Mass Spectroscopy Identification of are Shown by Different Colored Arrows and Text, with the Percent of Confidence in the Identification Given in Parenthesis.

In Figure 9, there is no indication of any significant contmination of the 1,1-difluoroethane standard. Potentially any chemical that was produced by exposing this standard to heat could be used as a fire indicator.

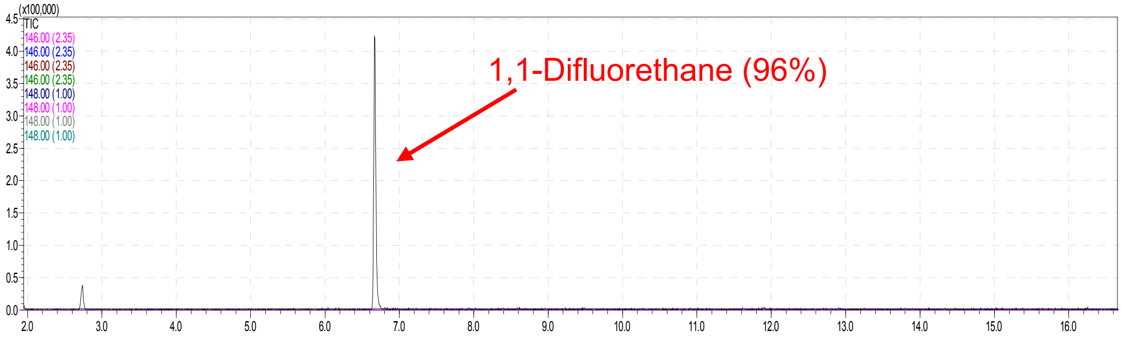

Figure 10
Gas Chromatogram of 1,1-Difluoroethane Standard
Mass Spectroscopy Identification of Peaks are Shown by Different Colored Arrows and Text, with the Percent of Confidence in the Identification Given in Parenthesis

5.1.1 Summary of the Experimental Determination of Purity

The octafluorpropane, tetrafluoroethane, and C6-perfluoroketone standards had small amounts of contaminants that would have to be taken into account if any of these standards are to be used as a FIG. The 1,1,1,3,3,3-hexafluoropropane and the 1,1-difluoroethane had no contaminants within the limits of detection by the gas chromatograph – mass spectrograph.

Incidental to the first set of experiments, it was noted that all five of the proposed FIGs could potentially be used as ordinary tracer gases in the study of mine ventilation systems. No detailed study of the applicability of the FIGs to ordinary tracer work was conducted, but gas chromatographic retention times were noted for the five FIGs; and for tetrafluoromethane, sulfur hexafluoride, and carbon dioxide. These retention times were noted for the Agilent H-P Plot Q column with conditions and temperature programming described above:

Tetrafluoromethane – 2.06 minutes
Carbon dioxide – 2.75 minutes
Sulfur Hexafluoride – 3.65 minutes
Octafluoropropane – 5.56 minutes
1,1-Difluoroethane – 6.69 minutes
1,1,1,2-Tetrafluoroethane – 6.78 minutes
1,1,1,3,3,3-Hexafluoropropane – 8.20 minutes
C6-perfluoroketone – 11.0 minutes

Figure 10 is the gas chromatogram of a mixture of 1000 ppm in air of each of these 7 potential tracer gases. Carbon dioxide is noted in the list because the Agilent H-P Plot Q column can separate it from the air peak, so it appears among the other peaks. As can be seen in this list, only the 1,1-difluoroethane and the 1,1,1,2-tetrafluoroethane interfere with each other. However, both of these peaks eluted after the temperature was ramped up from 40º C to 150º C, so further work might even allow for the separation of these two peaks. Even if one of these chemicals cannot be used with the other, there is still the possibility of deploying as many as six tracer gases at the same time.

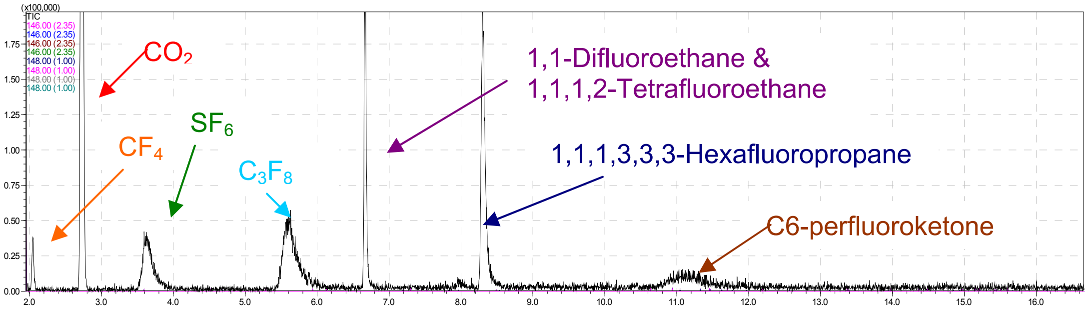

Figure 11
Gas Chromatogram of 7 Potential Fluorinated Tracers And CO_2
Mass Spectroscopy Identification of Peaks are Shown by Different Colored Arrows and Text

5.2 Auto-ignition of Potential FIGs

Generally, the second set of experiments consisted of exposing a known mixture of each FIG and air to heat in order to see if any reaction would occur. The basic chemical process is called auto-ignition. Auto-ignition is conducted by simply exposing a chemical to thermally produced radiation – no spark or flame is involved. Auto-ignition is more difficult to accomplish than ignition by flame or spark. As an example, the hydrocarbon heptane has a flash-point of -4º C, but heptane will not auto-ignite until 285º C. (Airgas, 2014) Auto-ignition was attempted, for the five potential FIGs, using an available clam-shell oven, which was manufactured by Supelco for use in high capacity gas purification for gas chromatographs. From the manufacturer's literature, the maximum temperature that the oven could achieve was 550° C. However, the stainless steel tube that was used to hold the potential FIG-air mixtures was only rated to 500° C. Therefore, 500° C was the maximum temperature to which the proposed FIGs could be exposed. A Variac was used to regulate the voltage to the oven, in order to regulate the temperature. A digital thermometer with a high temperature probe was used to measure the temperature that the oven achieved for a particular Variac setting. Any reaction of the proposed FIGs would take place in a reactor tube, heated by the oven. This reactor tube was a half inch outer diameter stainless steel tube with one end sealed with a stainless steel Swagelok cap, and the other end fitted with a Swagelok stainless steel union. The union allowed that end of the reactor tube to be sealed with a rubber septum; through which gases could be introduced into, or withdrawn from, the reactor tube by syringe. The layout of the equipment used for the experiments is shown in Figure 12 and Figure 13.

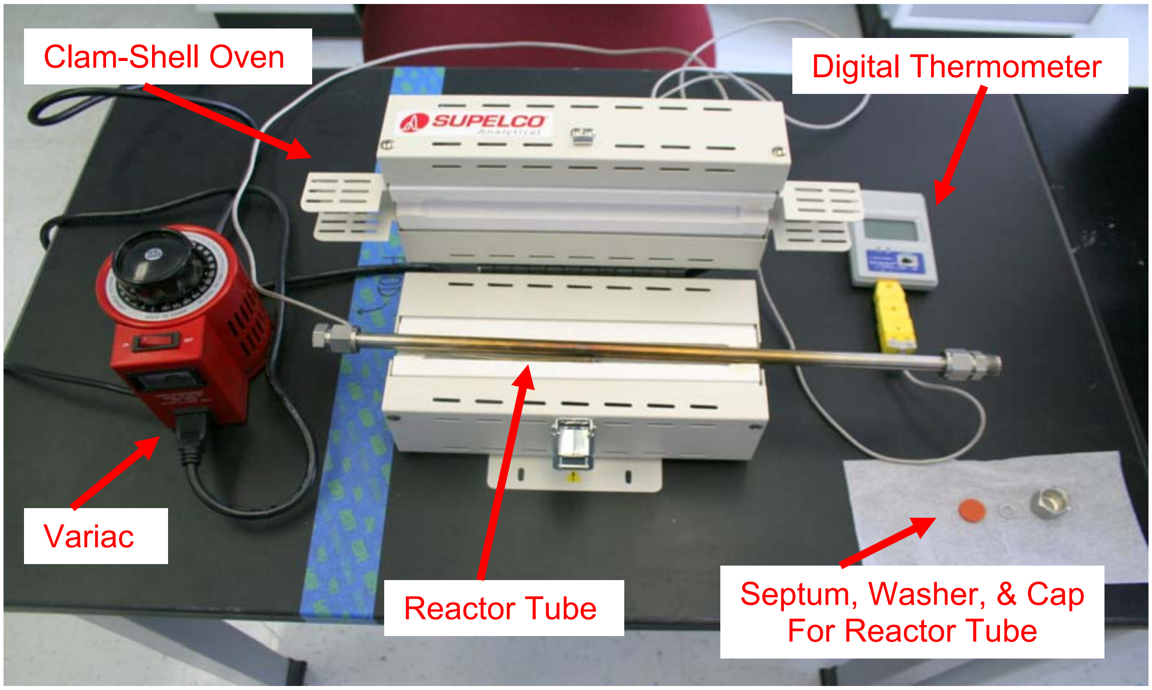

Figure 12
Layout of Equipment that was Used for Heating, And Attempting to React, FIGs

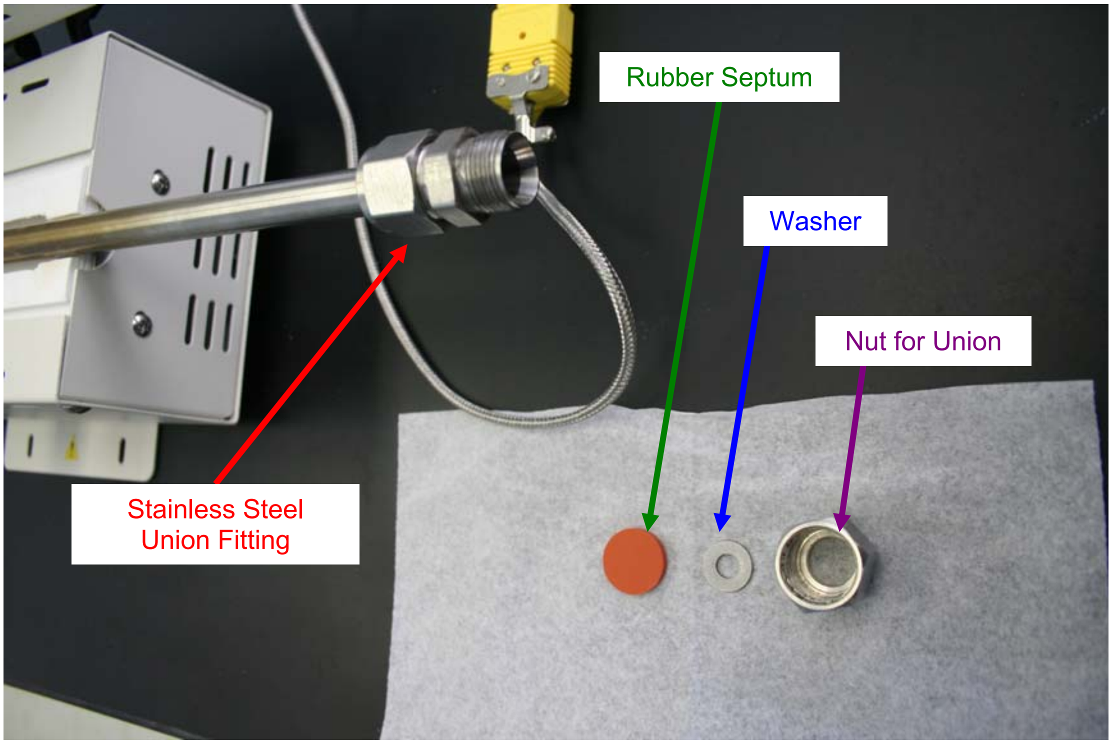

Figure 13

Details of the Union Fitting for Closing the Reactor Tube with a Septum

The Washer was First Placed Into the Nut, Then the Septum was Placed Inside the Nut, and Then the Nut was Screwed Onto the End of the Union Fitting.

Experiments were conducted by:

1. Closing the reactor tube by placing the metal washer and septum into the union nut, and then screwing the nut onto the union fitting on the end of the reactor tube.

2. With a syringe, an amount of the proposed FIG, to be heated, was introduced through the septum into the reactor tube. Calculations for the amount of gas to inject into the tube were based on a measured volume for the closed tube of 44.7 milliliters.

3. The reactor tube was placed in the oven, as shown in Figure 10, with the probe for the digital thermometer underneath the center of the reactor tube. The clam-shell oven was then closed.

4. The Variac was adjusted to yield the desired temperature for the desired time.

5. Using a syringe, a sample was withdrawn from the reactor tube for analysis using an available Shimadzu GCMS-QP2010 Ultra gas chromatograph-mass spectrograph (GC-MS).

Initially, each mixture of 5000 ppm of FIG in air was exposed, in the reactor tube, to 500º C for 20 minutes. Initial tests were done with a relatively high concentration of the FIG because any yields of a product could be low. The results of these tests are shown in the figures below. As can be seen from the figures, the octafluoropropane, 1,1,1,3,3,3-hexafluoropropane, and the 1,1,1,2-tetrafluoroethane did not react. However, the C6-perfluoroketone, and the 1,1-difluoroethane did react – each yielding a novel combustion product.

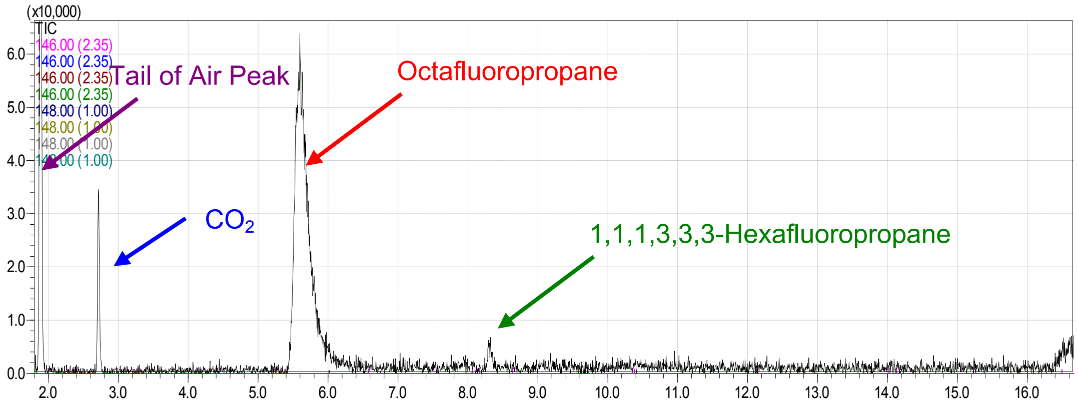

Figure 14

Gas Chromatogram of 5000 ppm of Octafluoropropane In Air, Heated to 500ºC for 10 Minutes

All Peaks Identified by Mass Spectrometry.
All Peaks Are the Same as the Octafluoropropane Standard Shown in Figure 6.

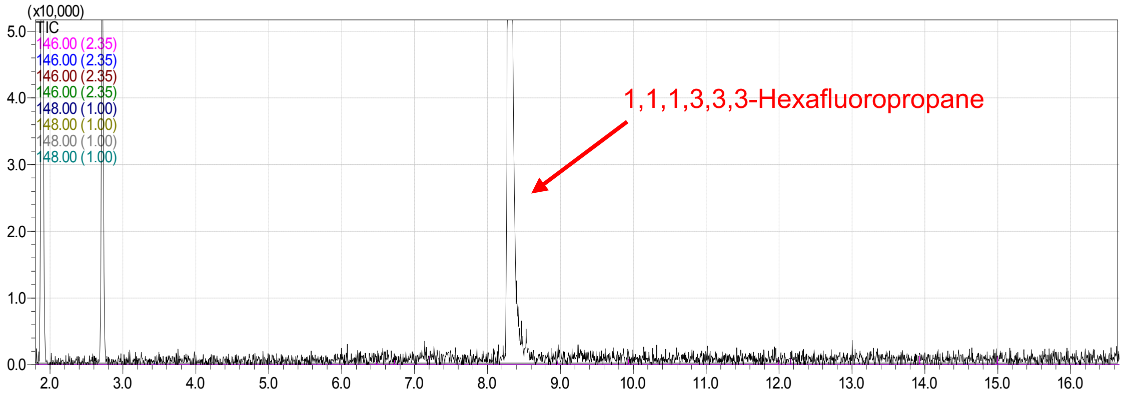

Figure 15

Gas Chromatogram of 5000 ppm of 1,1,1,3,3,3-Hexafluoropropane In Air, Heated to 500ºC for 10 Minutes

All Peaks Identified by Mass Spectrometry.
All Peaks Are the Same as the Hexafluoropropane Standard Shown in Figure 7

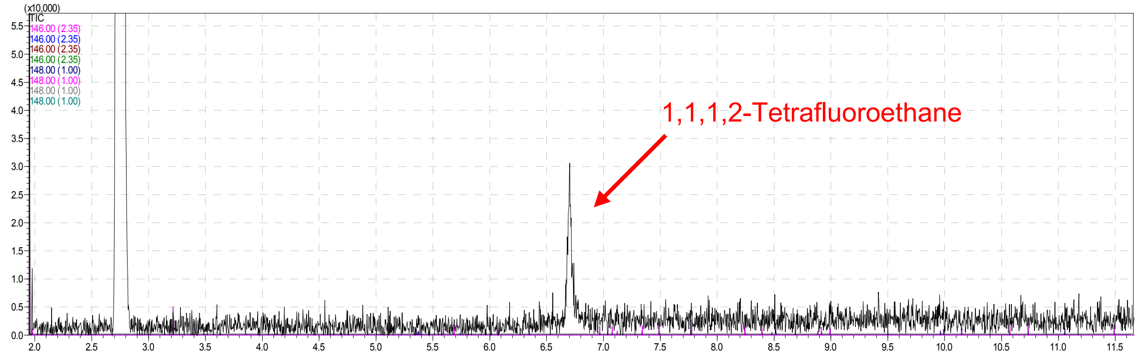

Figure 16

Gas Chromatogram of 5000 ppm of 1,1,1,2-Tetrafluoroethane In Air, Heated to 500ºC for 10 Minutes

All Peaks Identified by Mass Spectrometry.
All Peaks Are the Same as the 1,1,1,2-Tetrafluoroethane Standard Shown in Figure 8.

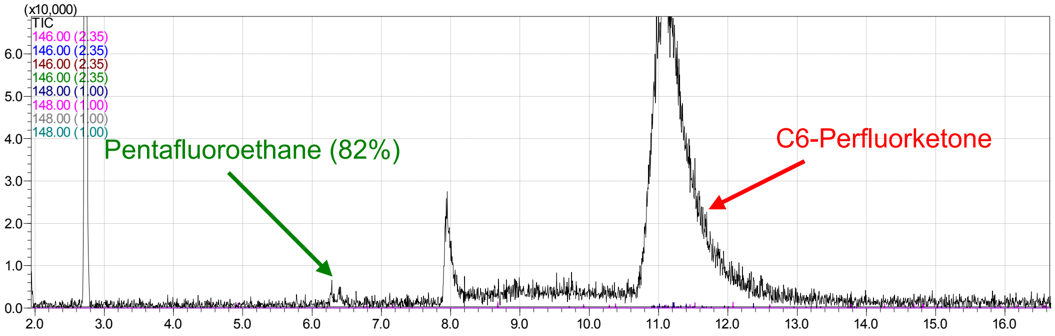

Figure 17

Gas Chromatogram of 5000 ppm of Headspace C6-Perfluoroketone In Air, Heated to 500ºC for 10 Minutes

All Peaks Identified by Mass Spectrometry.
All Peaks Are the Same as the C6-Perfluoroketone Standard Shown in Figure 9, Except the Peak Identified as Pentafluoroethane.

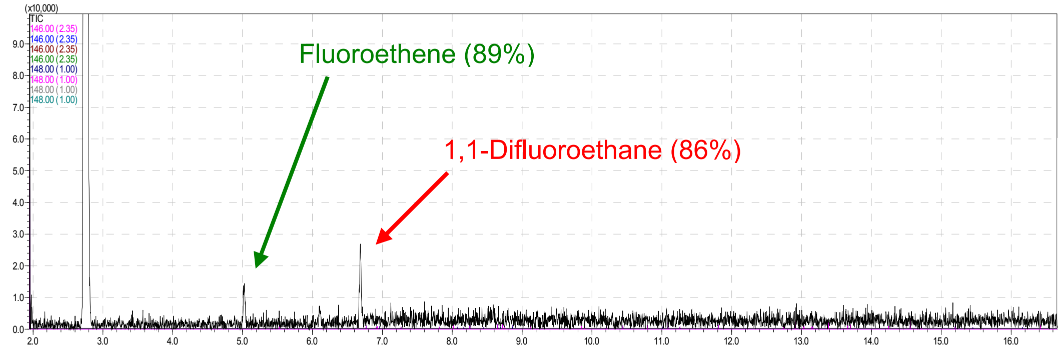

Figure 18
Gas Chromatogram of 1000 ppm of 1,1-Difluoroethane
In Air, Heated to 500ºC for 10 Minutes
All Peaks Identified by Mass Spectrometry.
All Peaks Are the Same as the 1,1,1,2-Tetrafluoroethane Standard
Shown in Figure 10, Except the Peak Identified as Fluoroethene.

5.2.1 Summary of the Auto-ignition of Potential FIGs:

C6-perfluoroketone and 1,1-difluoroethane auto-ignited at, or below, 500ºC. Octafluoropropane, 1,1,1,3,3,3-hexafluoropropane, and 1,1,1,2-tetrafluoroethane did not auto-ignite at, or below, 500ºC. However, it is important to keep in mind that all of the three compounds that did not auto-ignite, in these tests, will ignite at some temperature that is indicative of fire, when exposed to an open flame. After-all, these compounds are deployed as fire-extinguishants. They would not be successful fire-extinguishants if they did not break-down, when exposed to fire, into chemical radicals that would interrupt the chemical chain-reaction of the fire, and put the fire out. The question left unanswered is whether or not they would yield a novel product of combustion. Auto-ignition is a more difficult method of producing a chemical reaction than the use of an open flame or spark.

Accordingly, C6-perfluoroketone and 1,1-difluoropropane would be expected to undergo a chemical reaction at significantly lower temperatures in the presence of an open flame or spark. In addition, it is possible that one, or both, of them would yield different combustion products with an open flame, or spark, than they yielded by auto-ignition.

5.3 Determination of Auto-Ignition Temperature:

For the two FIGs that reacted at 500ºC, an attempt was made to determine the lowest temperature of reaction. Only a rough determination could be made because of the equipment, and also because of the nature of auto-ignition. With respect to equipment, the Variac dial which was used for setting the voltage to the oven did not allow for precise temperature settings. Dial settings apparently did not reproduce voltages exactly; and, as a consequence, the oven temperature was difficult to reproduce exactly. Several adjustments were typically necessary for any one test, with temperatures sometimes wandering as much as five degrees above the desired setting. The chemical process of auto-ignition can be affected by conditions that can be difficult to reproduce, such as coatings due to oxidation forming on the inside of the reaction tube – a likely complication in these tests. Auto-ignition can also be affected by such factors as the material the reaction vessel is made out of, and how large the vessel is. Smaller reaction vessels will yield higher auto-ignition temperatures. The ASTM standard method for determining auto-ignition temperatures uses a 500 ml glass flask. (ASTM, 2013)

The attempt to reproduce the auto-ignition of C6-perfluoroketone was an example of the potential difficulties in reproducing an auto-ignition reaction. In the first test to try to auto-ignite that compound, samples were taken from the reaction tube at 300º C and at 450º C. At 300º C, there was no evidence of any reaction; however, at 450º C there was clear evidence of a reaction. When the first attempt was made to reproduce this reaction, no change was observed at 450º C. The temperature of the oven had to be raised to 500º C before signs of a reaction were observed. In a follow-up attempt, no reaction was observed at 500º C. The reactor tube was then brushed out with a cylindrical brass brush, and the test was carried out yet again, yielding a reaction that was observed at 500º C, as illustrated by Figure 17 above. C6-perfluoroketone apparently auto-ignites somewhere from 450º C to above 500º C. Closer reproducibility would require a better definition of all the variables affecting auto-ignition. It might be noted that, in the real world of an underground coal mine fire, a good definition of all the pertinent variables would likely not be known.

Several tests were run on 1,1-difluoroethane to see if the minimum temperature for auto-ignition could be better defined for this compound. In the first set of tests, this compound was observed to show no sign of a reaction when heated to 400º C, but it did show the production of fluoroethene when it was heated to 500º C. Another test was run, starting at 400º C, with the plan to turn the temperature up in approximately 25º C increments (given the difficulty in controlling the temperature setting too closely) to 500º C in order to determine more closely the auto-ignition temperature. At 400º C, a 10 uL sample from the reaction tube was taken by syringe. When the sample was analyzed by the GC-MS, a reaction had already occurred.

Accordingly, another test was run with a starting temperature of 200º C. No reaction was detected at 200º C, and the temperature was increased by 50º C until there was evidence of a reaction at 350º C. The spectrogram of the sample that was taken from the reactor tube after 350º C had been achieved for ten minutes is shown as Figure 19.

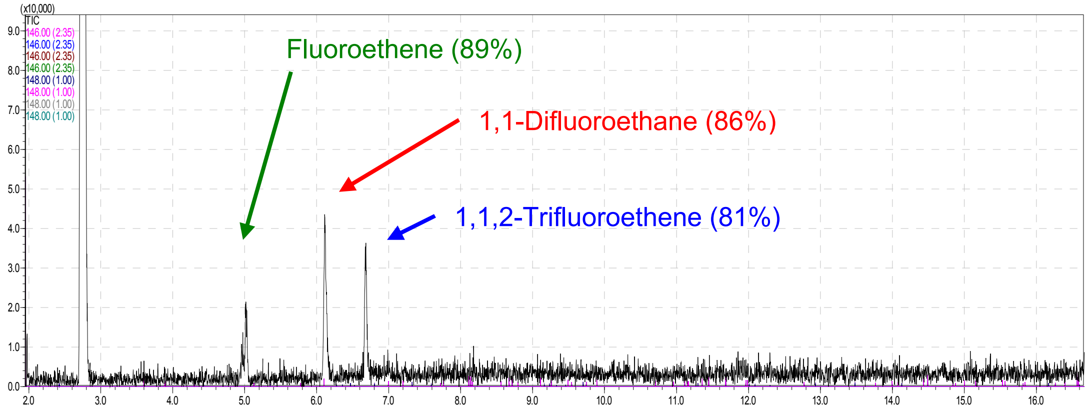

Figure 19
Gas Chromatogram of 1000 ppm of 1,1-Difluoroethane
In Air, Heated to 350ºC for 10 Minutes
All Peaks Identified by Mass Spectrometry.

This test produced another peak – 1,1,2-trifluoroethene – than the first test that was conducted at 500º C (Figure 18). Apparently, the reaction of 1,1-difluoroethane, with respect to products, can have different yields depending on the temperature and the amount of time that reactor tube is heated, and at what time the reactor tube is sampled. That would be possible, given that the temperature rise for these experiments were adjusted by hand. No two tests were exactly the same as far as how long the FIGs were exposed to different temperatures.

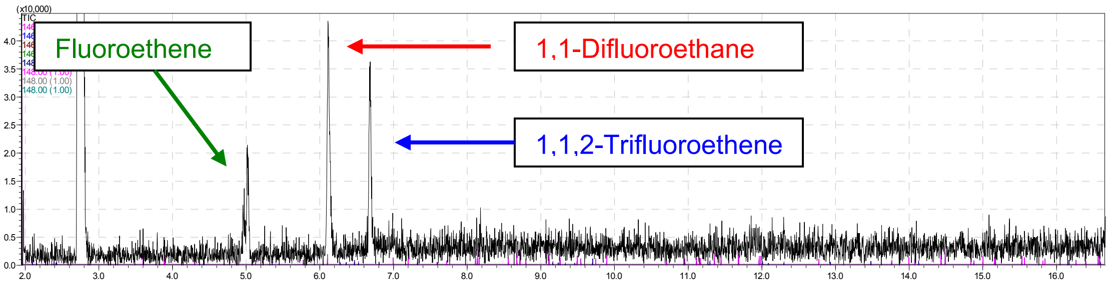

Figure 20

Enlargement of Gas Chromatogram of 1000 ppm of 1,1-Difluoroethane In Air, Heated to 350ºC for 10 Minutes

All peaks Identified by Mass Spectrometry

Furthermore, although no sensitivity tests were run for 1,1-difluoroethane, the peaks for that compound and for the reaction products are distinct, with a starting concentration for the 1,1-difluoroethane of 1000 ppm; and with a sample volume of 10 ul, that was split at a ratio of ten to one.

Figure 20 is the same as Figure 19, except the chart has been magnified to show the peaks and background noise better. Figure 20 was used to visually determine the signal to noise ratio for this run. The signal to noise ratio for each of the product peaks was determined by dividing the measured height of each of the two product peaks by the measured height of the highest background peaks immediately adjacent to each product peak. For the fluoroethane peak, the peak height is 22,000 units, and the highest noise peaks immediately adjacent have a height of 7,000 units; yielding a calculated signal to noise ratio of 3.1. For the trifluoroethene peak, the peak height is 37,000 units, and the highest noise peaks immediately adjacent have a height of 9,000 units; yielding a calculated signal to noise ratio of 4.1.

All of these factors raise the possibility that the starting concentration for 1,1-difluoroethane might be reduced by at least a factor of ten – maybe more – because the split ratio of 10:1 used for the injections into the gas chromatograph for this study could easily be reduced to splitless. This does not even take into account specifically targeting the reaction products with the mass spectrometer.

An experiment was also run with C6-perfluoroketone at a starting concentration of 1000 ppm in air, as opposed to the initial experiments at 5000 ppm. The results are shown in Figure 21.

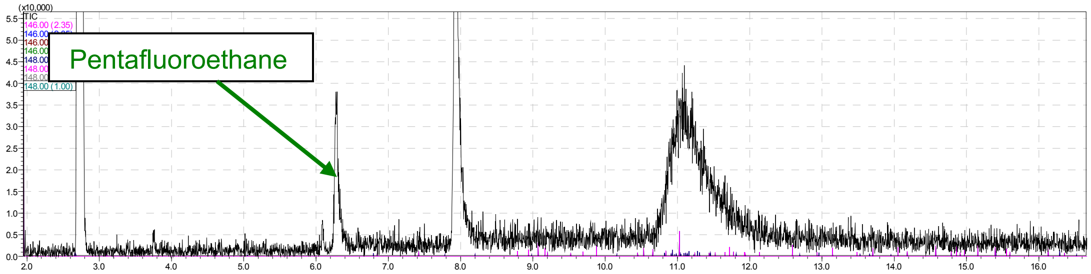

Figure 21

Gas Chromatogram of 1000 ppm of Headspace C6-Perfluoroketone In Air, Heated to 500ºC for 10 Minutes

All Peaks Identified by Mass Spectrometry.

Figure 21 can be used to calculate a signal to noise ratio for the pentafluoroethane product peak. The pentafluoroethane peak has a height of 38,000 units, and the immediately adjacent noise peaks have a maximum height of 8,000 units; yielding a signal to noise ratio of 4.75. Since the run in Figure 21 was conducted with the standard protocol of splitting the 10 ul injection at a ten to one ratio, it is reasonable to assume that C6-perfluoroketone could be practically used as a FIG at a concentration of 100 ppm.

5.3.1 Summary of the Determination of Auto-Ignition Temperature:

Although an exact auto-ignition temperature for C6-perfluoroketone and 1,1-difluoroethane could not be determined, in part because a recognized, standard procedure was not followed; a rough range of temperatures could be determined. Approximate auto-ignition temperatures are probably sufficient. Although more precise data could be obtained at considerable expense, the variables present in a mine setting would not match any standard experimental setting anyway.

C6-perfluorketone apparently auto-ignites, in the reactor tube that was used, at about 500º C, yielding pentafluoroethane. C6-perfluoroketone apparently also yields 1,1,1,2,3,3,3-heptafluoropropane as a breakdown product, but that compound is also present as a contaminant in the original C6-perfluoroketone, and therefore cannot be used as an indication of fire. 1,1-Difluorethane apparently auto-ignites, in the reactor tube that was used, somewhere between 350º C and 400º C; and yielded fluoroethene consistently, and trifluoroethene under some conditions.

Chapter 6: Examples of Inaccessible Mine Fires: Potential Application of Fire Indicator Gases

Examples of inaccessible mine fires include the following:

1. Spontaneous combustion, or methane ignition, in a mined-out area, such as a longwall gob.
2. A mine area, or entire mine, that has been sealed to extinguish a fire.
3. Pillars in a mine.
4. Fires that occur in abandoned mines.

Fire indicator gases could potentially help in the evaluation of each type of example. This chapter reviews several mine fires, along with how FIGs might have been applied, were they field-ready at the time.

6.1 Examples # 1 and # 2 – A Fire in a Gob, and a Mine that is Sealed

Methane gas ignitions have occurred with some frequency in, or adjacent to, longwall gob areas. After an ignition, there usually is a question as to whether or not the ignition sparked a fire. If there are indications of a fire, which are not necessarily definitive, a portion of the mine, or the entire mine, is sealed. When a mine area, or an entire mine, is sealed to extinguish a fire, there are frequently problems with obtaining information on the status of the fire area that is needed in order to determine when it is safe to recover the mine. An example of all these problems occurred at the mine fire of 2007, in Consolidation Coal Company's Buchanan Mine Number 1, in Buchanan County, Virginia.

On the morning of July 9, 2007, shortly before 10:00 am, a series of underground shock-bumps and roof falls occurred in, or near, the 9 Right off East Mains longwall gob area. The bumps and roof falls caused a methane ignition in the gob area. Carbon monoxide readings climbed to significant levels at various locations in, and around, the 3 East gob. Nitrogen injection began on July 15 and continued until September 26th. At that time, nitrogen injection was stopped to allow evaluation of the mine atmosphere. Gas samples indicated that CO was still being produced, therefore nitrogen injection resumed on September 30th. The mine was sealed on November 27th. The 3 East gob area was monitored at 39 different boreholes until January 20th, 2008, at which time the oxygen level had remained low enough for a sufficient period of time that the decision was made to unseal the mine. Exploration by mine rescue teams began on January 29th, and was completed on January 31st, without detecting any problems. On February 17th, ventilation of the mine was reestablished. (Virginia Dept. of Mines, 2008)

This case suggests some questions that are common for a concealed mine fire. These questions include:

1. Is there a fire?
2. Where is the fire located?
3. What is the extent of the fire?
4. Is any effort to fight/contain the fire having any success?
5. When is it safe to reopen the mine?

For this particular example, the first question apparently was not answered by initial observations made by mine personnel within the first 3 hours after the shock-bumps. During these hours, some mine personnel were still travelling in the mine, taking gas readings and looking for signs of damage. Although the Virginia State Report does not specifically address the issue, it would appear that mine personnel may have been thinking that they experienced a methane ignition – therefore, the elevated CO readings – but that the ignition may not have resulted in a fire. The report only mentions continual monitoring for days, with the mine still actively ventilated. If that was the case, FIGs might have been advantageously employed – as described below – during the first few days after the shock-bump and ignition. FIGs may have yielded definitive evidence as to whether or not there was a fire.

Then, mine personnel decided that they were dealing with a fire when “Carbon monoxide readings climbed to significant levels and continued to fluctuate at various locations in and around the 3 East gob.” (Virginia Dept. of Mines, 2008, page 9) At that point in time, several days had passed since the initial event. The company had been making plans to try to inert the mine atmosphere in the gob area with nitrogen, but the question was: where to pump the nitrogen for best effect? Personnel had not been able to determine where the initial ignition had taken place (Question #2 above), and there was no clear indication as to what the extent of the spread of the fire during the several days of initial monitoring might be (Question #3 above). The 3 East gob was a large area – as shown in Figure 22. Each of the longwall panels is approximately 1000 feet wide. (Virginia Dept. of Mines, 2008, page 16). Again, the location and extent of the fire might be better defined with the use of FIGs, as detailed below.

Bumps and ignitions like this usually occur in the gob of the active longwall panel, or in the gob of the longwall panel that had been completed most recently. That was the eventual conclusion in this case, but some elevated CO readings and some signs of damage in the 3 East Mains outby the area of most recent mining apparently created some doubt. If the entire 3 East gob was potentially in doubt, the targeted application of FIGs to the gob could have helped narrow the site of any fire.

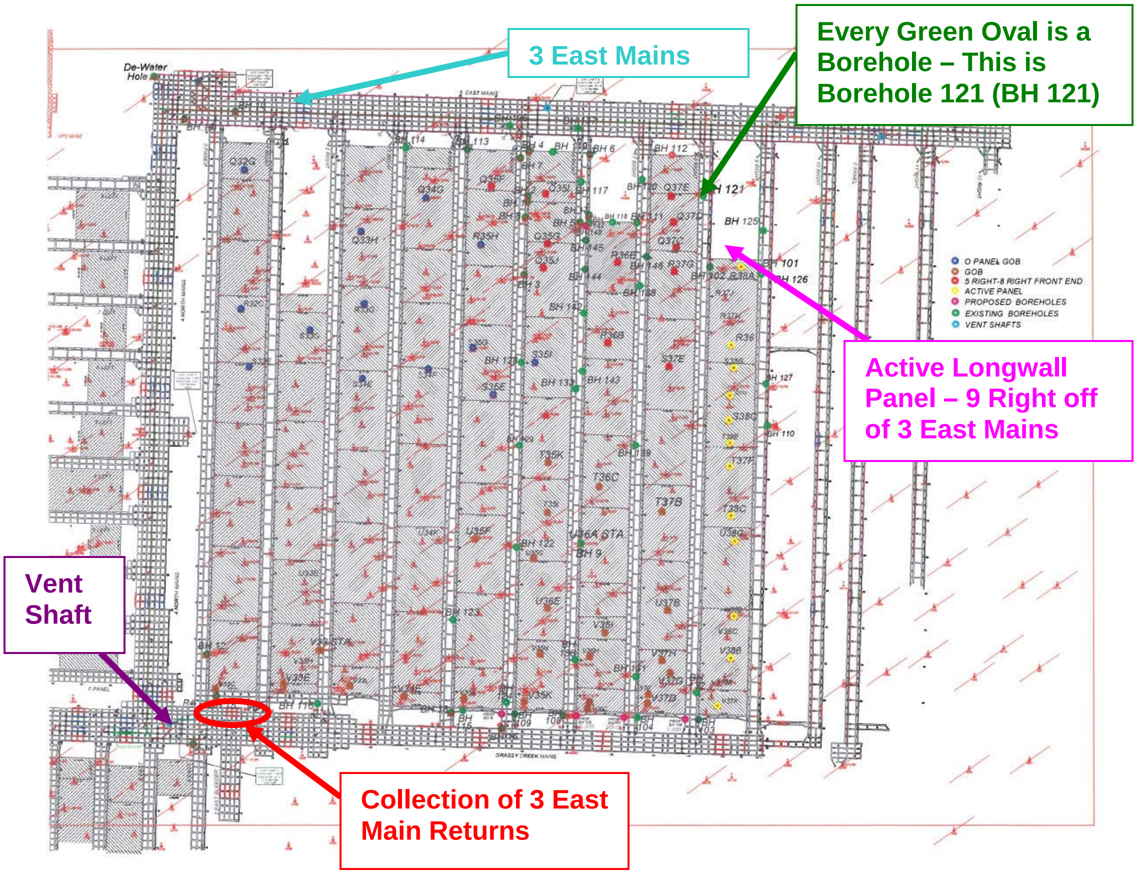

Figure 22
Map of 3 East Part of Buchanan Mine #1
(Virginia Dept. of Mines, 2008, page 16)

6.1.1 Question # 1 – Is There a Fire?

Ignitions can occur and generate CO gas, but not necessarily start a fire. If a coal fire is started, it can generate temperatures up to 1000°C. Laboratory experiments conducted as part of this study demonstrated that 1,1-difluoroethane and C6-perfluoroketone have auto-ignition temperatures of 500°C, or less. Basic chemistry dictates that these compounds would ignite, or decompose, into their distinctive break-down products at even lower temperatures in the presence of a spark or open flame.

During the first few hours after the ignition, while personnel were still traveling up and down 3 East Mains, trying to determine if there was a fire, and trying to determine approximately where the ignition took place; a FIG, such as 1,1-difluoroethane or C6-perfluoroketone, could have been introduced into the air flow, as the flow entered various areas of the gob. If multiple points of intake are available, as was the case for the 3 East gob of this mine, the FIG could be introduced into the intake air at points progressively further from the ultimate return sampling point. Such a progressive introduction would not only allow a definite determination as to whether there was a fire, but might also allow a better location of a fire within the gob. Generally speaking, personnel will not be in the mine for two or three hours after such events described here, and various boreholes would then be used. This mine had a lot of existing boreholes in the 3 East gob. Every green oval on the mine map, shown in Figure 22, is an existing borehole. To treat most of the 3 East gob, a FIG could be introduced into the mine down borehole number 121 (labeled in the upper right corned of Figure 22). Samples could then be taken periodically at a number of the boreholes that are located at the exits of each of the old longwall panels into the main returns

Air samples would be collected regularly in order to allow evaluation of the parent FIG and any break-down products that would appear in the return air-flow. Collection of air samples from the returns would have to be done remotely, using boreholes, because of the explosion hazard. Air samples could be collected by using tubing and air sample pumps. Small gas sample bottles, or vacutainers, could be used; since only one or two hundred microliters would be needed for analysis with a gas chromatograph.

The total air-flow ventilating the entire gob is an important parameter. Large gob areas in gassy mines, such as the 3 East gob, would typically have a total return air-flow on the order of 100,000 cubic feet per minute – within a factor of two. If different parts of the gob area can be tested separately, by using a combination of boreholes particular to a portion of the gob, then less total airflow would be involved in a test, and a lower amount of FIG would be needed for the test. Based on the laboratory tests discussed in Chapter 4 above, the intake air-flow should be initially dosed such that the concentration of a FIG would be about 100 ppm as the air travelled through any part of the gob where a fire might be. However, air-flow in the gob will be non-homogenous and diffusive. If one were to initially dose one minute of air-flow to a concentration of 100 ppm of 1,1-difluoroethane – a “slug” of air – this slug of air will diffuse as it travels through the gob. At a sampling point in the main returns, many minutes of air would be dosed with 1,1-difluoroethane – all off it at a concentration less than 100 ppm. There are so many variables, some of them case specific with respect to exact intake and exit points, that site specific knowledge would be necessary. A good starting point might be to plan on dosing one or two minutes of air-flow with 1000 ppm of 1,1-difluoroethane. If one minute is dosed, and the total air-flow is 100,000 cubic feet per minute (cfm); then 100 cubic feet of 1,1-difluoroethane would be needed. 100 cubic feet is equivalent to 2,832 liters, which equals 126 moles of an ideal gas. The molecular weight of 1,1-difluoroethane is 66; therefore, 8.3 kilograms, or 18.3 pounds of 1,1-difluoroethane would be needed. (126 moles x 66 = 8,316 g = 8.3 Kg) Dosing of the air-flow might be as simple as opening up the valve on a 20 pound cylinder that is set-up in the main air intake to the gob, if it were done by the mine personnel that were still underground during the first three hours after the ignition. Otherwise, it would have to be done by pumping the FIG down a borehole.

It should be noted that the general calculation for the amount needed is the same for C6-perfluoroketone as for 1,1-difluoroethane, except the molecular weight of C6-perfluoroketone is much larger – 316 grams per mole. Therefore, the amount of C6-perfluoroketone needed to dose 100,000 cubic feet per minute to 1000 ppm would be 126 moles x 316 grams per mole = 39,816 grams, or 39.8 Kg. Another difference in the use of C6-perfluoroketone, other than the weight, is that C6-perfluoroketone is a volatile liquid at ambient temperatures. This property of C6-perfluoroketone may be an advantage or a disadvantage in different circumstances, but it will mean that C6-perfluoroketone will have to be handled differently to dose a given airflow.

Another factor that will necessitate experimentation involves exactly how much breakdown product of the 1,1-difluoroethane will be produced for detection. Among other factors, the concentration of the breakdown product in an air-flow downwind of a fire will depend on the size of any fire, how much airflow is exposed to the fire, and the typical yield of the breakdown reaction. Typical reaction yields could be determined in the laboratory, but were not a part of this study. The size of a particular fire, and the exact location of a fire with respect to air-flow paths, are specific to each case; and will be unknowns in any case. Adjustments will have to be made during field use. When using FIGs, false negatives are a possibility, due to diffusion and dilution. But false positives are very unlikely. In cases where there is a known fire, and FIGs are being used to try to locate the fire more precisely, negative results might call for a higher concentration of the FIG to be introduced into the intake airstream. Also, more sensitive settings could be used on the mass spectrograph detector than were used for the laboratory experiments described above. The mass spectrograms produced for this study were made in a general scan mode, whereas, the mass spectrograph could be run in a selective mode – just looking for the signature of a particular breakdown product – with a 100 fold increase in sensitivity.

6.1.2 Questions # 2 and # 3 – Where is the Fire, and What is the Extent of the Fire?

Company personnel did not definitely determine that they were dealing with a fire, and they did not determine an approximate location of the ignition, during the first couple of hours. The entire 3 East gob could not be ruled out, based on initial CO gas measurements. Eventually, toward the end of three hours after the original ignition; some evidence, in the form of elevated CO readings and in the form of a second ignition (which jeopardized two personnel), indicated that there was a fire, and that the fire area was likely the 7 Right gob or the 8 Right gob. (Virginia Dept. Mines, 2008, p. 8) But this evidence was still not conclusive. The use of FIGs might have clarified these two questions.

The decision was then made to try to inert the atmosphere in the gob by nitrogen injection. Apparently, the mine was still ventilated, since the Virginia State report states that the mine was not sealed at this time. Company personnel had no way to gauge any spread of the fire before, and during, the nitrogen injection. The fire had presumably been burning for six days before the nitrogen injection started. When nitrogen injection was briefly stopped on September 26th, personnel concluded that CO was still being produced; but this conclusion was based on observations made from boreholes that ringed the perimeter of the large gob area. The cited Virginia State report did not provide details as to how conclusive the determination of continued production of CO was. An obvious question would be: was the CO detected at this time the result of a continuing fire, or the result of a large build-up of CO in a large gob area? When the company concluded that CO was still being produced, the mine was finally sealed, and remained sealed for almost two months. After almost two months, personnel concluded that oxygen levels had remained low enough for a long enough period of time that combustion had likely ceased. The mine was then successfully recovered.

If mine personnel had been able to answer questions #2 and #3, efforts to control the fire by inerting the atmosphere with nitrogen might have been successful. If existing, and supplemental, boreholes were spaced throughout the gob, and there was communication between the boreholes; then FIGs could potentially help define the location and extent of a fire. If the mine was still ventilated, then a FIG would have to be introduced down a borehole that is toward the intake side of the eventual planned sampling borehole. If the mine ventilation has been stopped, a FIG could be introduced into a centrally located borehole, and then surrounding boreholes could be sampled in order to determine if the FIG, and any breakdown products, showed up.

The company’s area of primary concern is shown in a bright pink oval on the map in Figure 23. The map in Figure 23 is the right part of Figure 22. Existing boreholes are shown on the mine map as green ovals – as the green oval that the bright green arrow is pointing to. As can be seen in Figure 23, there were numerous boreholes in, and around, the area of concern.

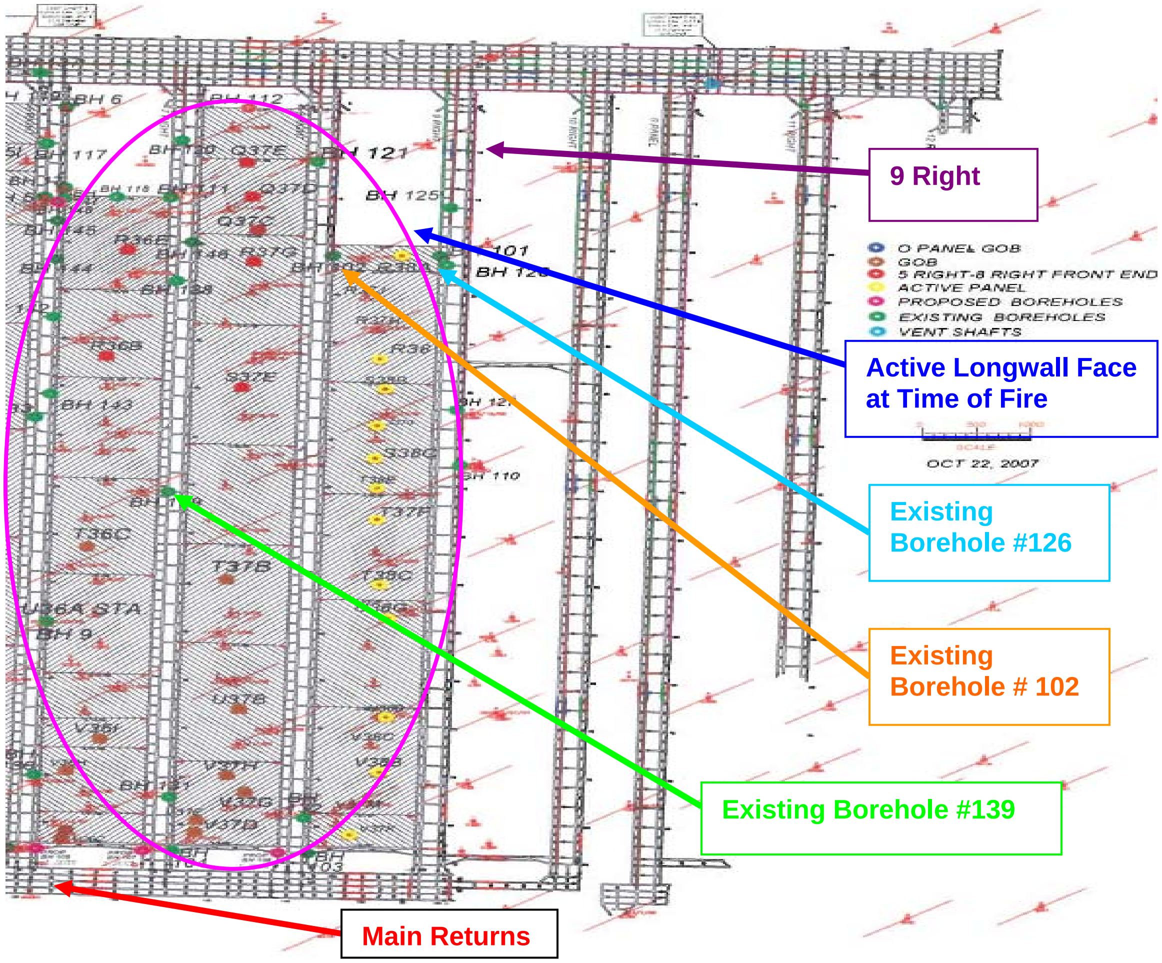

Figure 23

An Enlargement of the Right Side of Figure 22

Showing, in the Pink Oval, the Primary Area of Concern Where the Fire Was Probably Located

In this example, a FIG, such as 1,1-difluoroethane, could be introduced down borehole #126; and sampling for the FIG and the breakdown products could occur at boreholes downwind, at the end of adjacent, mined-out longwall panels. This process would obviously be aided if the ventilation controls in 9 Right had not been damaged by the ignition. If the ventilation controls were not damaged, less amount of 1,1-difluoroethane than the 18.3 pounds approximated above might be used. Pumps and tubing would be used to introduce the FIG down one borehole, and recover air samples for analysis up other boreholes. Again, small samples would be collected in gas sample bottles or vacutainers. Analysis would be done by gas chromatograph.

This process would probably be easier, and potentially more meaningful, if it were conducted with the mine ventilation stopped. Then, borehole fans could be used to better direct the airflow through areas of interest. A borehole suction fan could be set up on borehole #139, and used to draw air samples. It might be possible to put 1,1-difluoroethane down boreholes in sequential steps radiating away from borehole #139, to better identify the location and extent of any fire. In addition, introduction of the FIG could start with boreholes on the left side of the pink oval in Figure 23, where the fire is less likely to be; and progress to boreholes around the top of the oval and to boreholes located to the right side of the oval, where the fire is more likely to be. Putting a FIG down borehole #102 could be especially informative, by providing information as to whether or not any fire that may have started in the current longwall gob had progressed into the previous longwall gob.

6.1.3 Question # 4 – Is Any Effort to Fight/Contain the Fire Having Any Success?

After injecting nitrogen into the mine from July 15th to September 26th, company personnel halted the injection for several days in order to see if the nitrogen injection had been effective. Presumably, the mine was still being ventilated, since the state report mentions that the mine was not sealed until November 27th. Company personnel judged that CO was still being produced, therefore, there was still a fire; and they resumed nitrogen injection on September 30th. The state report contains no other information about the efforts to combat the fire with nitrogen, except to note that the mine was sealed on November 27th. There is no mention of any further evaluation of the mine fire between September 30th and November 27th.

Apparently, four months of nitrogen injection was ineffective. Apparently, the only way that company personnel had to judge whether the nitrogen was effective was to stop the nitrogen injection, and allow air back into the fire zone. Letting air back into the fire zone might have undone some of the good that the nitrogen might have done. Again, FIGs could have helped, by giving better information about the effectiveness of the nitrogen.

There is good evidence that halogenated hydrocarbons will form distinctive breakdown products in a nitrogen atmosphere when exposed to heat associated with fire. Yu, et al, in a paper previously cited in Chapter 4, demonstrated that even a simple halogenated hydrocarbon, like halon 1211 ($CBrClF_2$), will undergo thermal decomposition in a nitrogen atmosphere at temperatures between 500C and 700C, yielding a number of distinctive products. (Yu et al, 2005, p. 134) FIGs could likely be used to monitor the effectiveness of the nitrogen much more frequently than once in two months. This could be done without interrupting the nitrogen flow for several days, and giving the fire a chance to rekindle. Whichever borehole had been judged to be closest to the fire could be used to introduce the FIG into the fire area. Any immediately adjacent borehole(s) could be used to collect samples, with sample pumps and tubing. Again, analysis could be by gas chromatography. Since only a portion of the gob would be involved in such a test, much less than 18.3 pounds of 1,1-difluoroethane would be needed per test. If an initial test were done before, or at the beginning of, the inerting effort, a baseline could be established. If subsequent tests, over a period of days or weeks, showed that the nitrogen was not having the desired effect, different action could be taken much sooner than four months.

6.1.4 Question # 5 – When is it Safe to Reopen the Mine?

FIGs could also be used to confirm that the fire is out. When a mine has been sealed for a period of time to extinguish a fire, as Buchanan Mine Number 1 was, 1,1-difluoroethane could be introduced down a borehole that was indicated as being relatively near the fire area. Nearby boreholes could be sampled periodically for the 1,1-difluoroethane and its breakdown products. Sampling pumps, or more likely induced draft fans, as discussed below in section 6.2, could be used for the sampling. If breakdown products of 1,1-difluoroethane were observed at the nearby boreholes, that would be positive evidence that the fire area was still above 350°C. The fire might rekindle if ventilated.

The FIG based monitoring of the fire area could be continued during reopening of the mine. In the case of the Buchanan Mine Number 1, the decision was made to attempt to reopen the mine when oxygen concentrations in the fire area had remained low enough, for a long enough period of time, that it was thought the fire must be extinguished. At that time, mine rescue teams were first sent in to explore the general area where the fire was thought to have been. When the mine rescue teams reported no evidence of an active fire, the mine was re-ventilated without incident. However, sometimes when sealed fire areas are examined by mine rescue teams and re-ventilated, fires do rekindle. The original fire area is still inaccessible. There is still a large reservoir of combustion products in the mine atmosphere. If the mine is re-ventilated, and the fire does rekindle, the whole process of sealing and waiting starts anew. Hot, smoldering fires would breakdown FIGs. Monitoring of a sealed fire area with FIGs could provide evidence that there is, or is not, a smoldering fire. When a sealed fire area is being reopened and re-ventilated, continued monitoring of the area with FIGs could provide an early warning if there is a rekindling fire. False negatives would be a possibility if not enough of a FIG were used. However, the relatively small mine area that would be monitored, and the relatively low volume of air produced by induced draft fans, should make it possible to put fairly large concentrations of a FIG into borehole airstreams. If FIGs were used in a way that caused concerns about false positives, due to remains of breakdown products in the atmosphere due to an earlier test, a different FIG could be used for a subsequent test.

Finally, all the examples of FIG use discussed in connection with the Buchanan Mine Number 1 example would have to be carried out under a plan, approved by the Mine Safety and Health Administration and the State of Virginia, to address closure orders. The use of FIGs should be allowed, given that they are considered to be nontoxic. Concentrations would be relatively low – no higher than 1000 ppm to 10,000 ppm. Their use would occur with no men in the mine; except, possibly, during mine rescue team explorations. That could be avoided if necessary.

6.2 Fires That Occur in Abandoned Mines

Ann Kim, in a 2004 paper titled "Locating Fires in Abandoned Underground Coal Mines," notes that such fires are "a relatively common occurrence in coal-producing areas." In her paper, she explains a methodology to approximately locate burning areas in abandoned mines using hydrocarbon gas ratios, boreholes, and suction pumps. The hydrocarbon gas ratio is an empirical formula based in part on the previous work conducted on the desorption of light-weight hydrocarbons, discussed in Chapter 2 above. For this paper, Kim developed the hydrocarbon gas ratio:

$$R_1 = \frac{[1.01(\mathrm{THC}) - (\mathrm{CH_4})]}{[(\mathrm{THC}) + c]} \times 1000$$

In this formula, (THC) equals the concentration of total hydrocarbons, in ppm; (CH_4) equals the concentration of methane, in ppm; and "c" equals a constant of 0.01 ppm in order to eliminate the possibility of dividing by zero. (Kim, 2004, p. 51) Laboratory tests were used to determine what value of the ratio of total hydrocarbons to methane corresponded to fire conditions. Based on these tests, Kim deduced that an R_1 value of zero to 50 corresponded to "normal" coal temperatures. An R_1 value of 50 to 100 corresponded to "possibly heated coal," and an R_1 value greater than 100 corresponded to “heated coal.” (Kim, 2004, p. 50)

Light-weight hydrocarbon gas measurements are obtained from abandoned mine-works by applying an “induced-draft fan” to closely spaced boreholes that penetrate the old works. Kim notes that there are some assumptions associated with this methodology. These assumptions include:

1. Changes in the relative concentrations of hydrocarbon gases underground are due only to the presence or absence of heated coal.
2. A sufficiently large vacuum applied to underground regions will cause the gases desorbed from heated coal to flow toward the point of suction.
3. Underground gas flows follow a straight line path toward the suction point. (Kim, 2004, p. 61)

A schematic of an ideal layout of the fan, and boreholes, is shown in Figure 24.

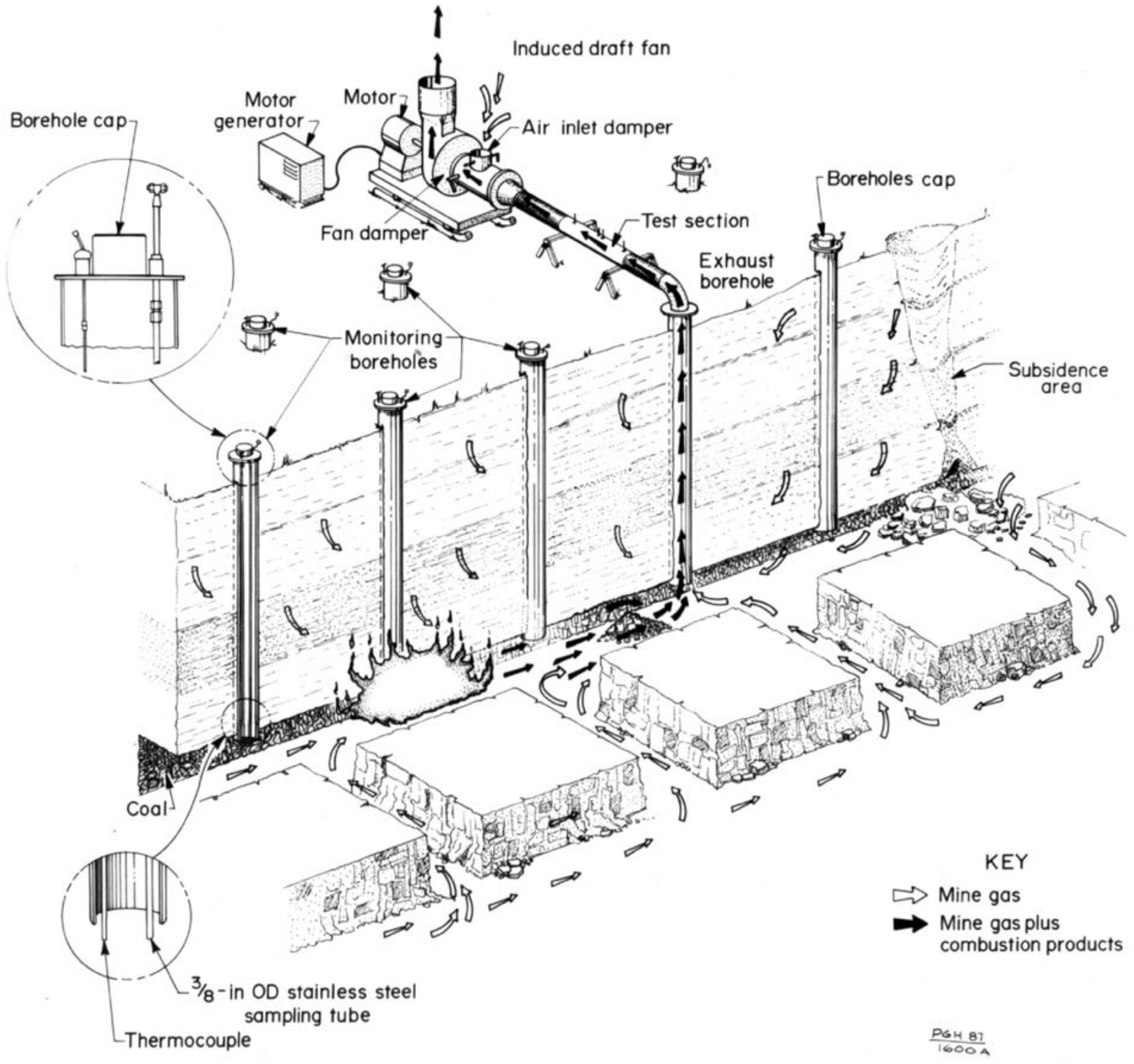

Figure 24
Schematic of an Ideal Layout for Locating a Fire in an Abandoned Coal Mine
(Kim, 2004, p. 50)

Sampling for hydrocarbon gases is not just conducted at the inlet of the induced draft fan, but is also conducted at surrounding boreholes; by the use of gas sampling pumps and tubing. Vacutainer samples are collected and analyzed for light-weight hydrocarbon content, and this analysis is then used to determine which boreholes are showing heated coal. Kim noted that the induced pressure effects could be detected several hundred yards from the induced-draft fan, which was rated at 2920 cubic feet per minute. The results of this technique, conducted at the abandoned Percy Mine in Fayette Co., PA; are shown, for each borehole sampled, in Figure 25.

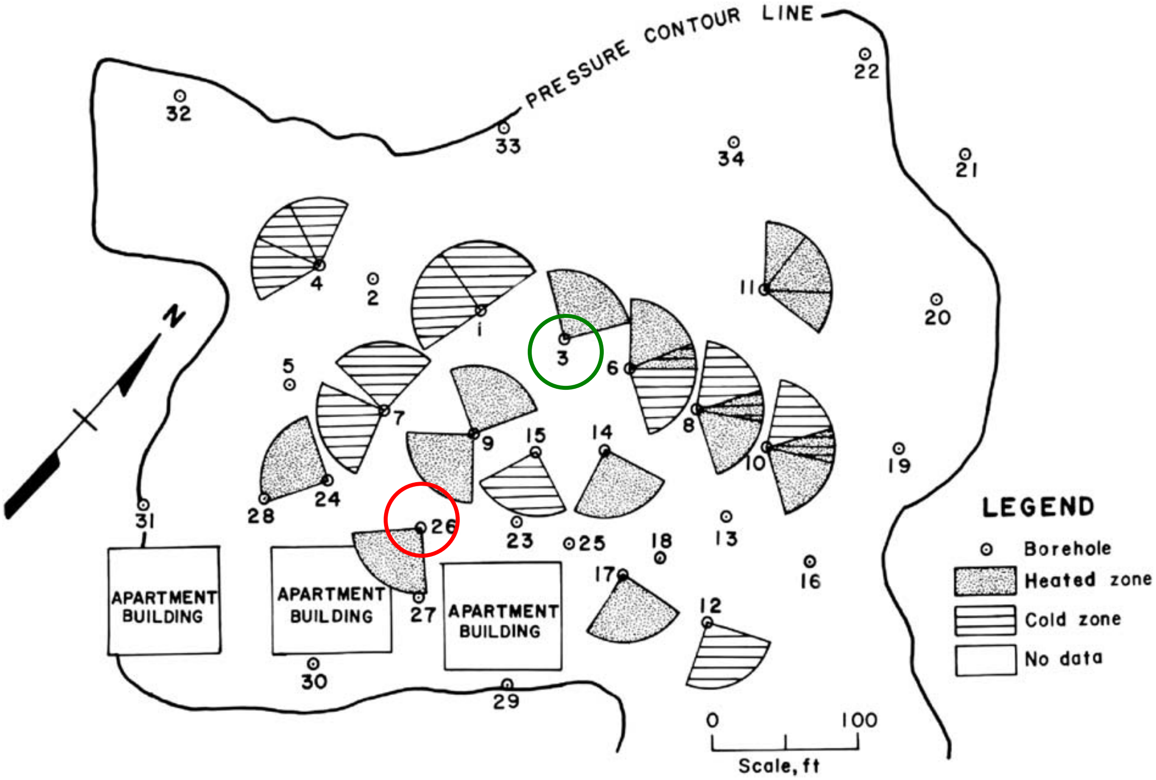

Figure 25

Plot of Boreholes

With the Determination of Heating Results For
Two Different Suction Points – Boreholes #26 and #3
(Colored Circles Added to Accent Boreholes Referred to in Text)
Percy Mine, Fayette Co., PA
(Kim, 2004, p. 53)

Instead of interpreting hydrocarbon ratios based on laboratory tests, the use of FIGs in a case like this could be more definitive. For the scenario pictured in Figure 25, if the objective is to determine if the abandoned mine fire is encroaching on the apartment buildings, a test could be conducted on a line of boreholes immediately in front of the buildings. The induced draft fan could be set up on borehole #12. A FIG could be introduced, by a tube, down the borehole that is in front of the buildings and is farthest away from #12, and still has communication with #12. Communication is established when the fan is turned on, and a pressure drop is observed in the distant borehole. If borehole #31 has communication with borehole #12, then the FIG could be put down #31. Then, sample pumps would be used to sample all the boreholes roughly in line with boreholes #12 and #31 – in this case, boreholes #28, #24, #30, #26, #27, #29, #23, #25, and #17. Any borehole that the FIG shows up in has communication with borehole #12 and borehole #31. Since some of these boreholes are not in a straight line between #12 and #31, this procedure would serve as a check of Assumption #3 listed above. Old mine entries and pillar lines may divert flows from straight lines. Of course, samples collected at all these boreholes in which the FIG showed up would also be tested for the breakdown product. If boreholes #28, #24, #26, and #27 had the FIG show up, but no breakdown product; and borehole #23 had both the FIG and the breakdown product show up, it would be a positive indication that there was a fire between #26 and #23.

6.3 Fires That Occur in Coal Mine Pillars

D.C. Panigrahi and R.M. Bhattacherjee, in a 2004 paper titled “Development of Modified Gas Indices for Early Detection of Spontaneous Heating in Coal Pillars,” note that pillar fires are “very common” in some of the coal fields of India; due, in part, to the susceptible nature of the coal to spontaneous combustion. They also noted that pillar fires tend to occur in pillars:

1. Subjected to high ventilation pressures, as in pillars separating main intake and return airways.
2. Near geologically disturbed zones.
3. Within 2 to 3 meters of the surface of the pillar. (Panigrahi and Bhattacherjee, 2004, p. 376)

Presumably, these coal pillars are fractured, and permeable enough, such that large pressure differences drive enough airflow through portions of the pillar to be optimal for the development of spontaneous combustion.

For this paper, the authors drilled a set of small diameter boreholes 3.5 meters deep into two different coal pillars. The layout of the boreholes is shown in Figure 26. Surprisingly, boreholes were not drilled adjacent to the stoppings or doors. A pair of tubes, for sampling, was then sealed into each borehole by grouting the mouth of each borehole, such that the inlet for each pair of tubes was isolated inside the pillar; and samples of gases from inside the pillar could be withdrawn for analysis. The authors then sampled and analyzed for CO, CO_2, O_2, and CH_4, for a time period of up to 35 days. They then plugged those gas concentrations into the usually gas indices, such as Graham's Ratio, Young's Ratio, and the CO/CO_2 Ratio to see if they could determine whether or not spontaneous combustion was occurring inside the pillars. They concluded that none of the ratios worked satisfactorily, and that the ratios needed to be adjusted to take into account the amount of CH_4, and the amount of blackdamp, in the gas analysis.

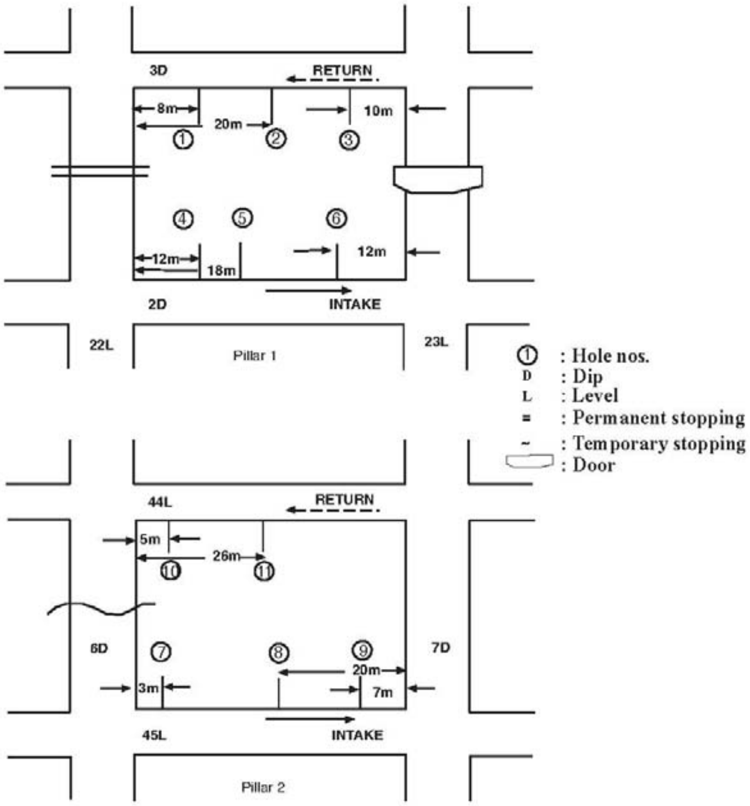

Figure 26

Layout of Boreholes in Coal Pillars Used to Check for The Development of Spontaneous Combustion

(Panigrahi and Bhattacherjee, 2004, p. 369)

A more straight-forward approach might be to employ the FIG technology. It has not been demonstrated yet that FIGs will breakdown and yield distinctive breakdown products in the range of 100C to 200C, a temperature range that would be most useful for detecting spontaneous combustion. But such temperatures are a distinct possibility. As noted earlier, compounds will breakdown at lower temperatures, in the presence of a spark or flame, than they do when they are just exposed to a large amount of heat: the auto-ignition situation. Acetone, which has an auto-ignition temperature of 465°C to 525°C (Wikipedia, 2014) could not be auto-ignited at 500C using the apparatus pictured in Figure 10 on page 75. The range of reported value – 465°C to 525°C – is a reflection of the difficulty in reproducing auto-ignition results. And yet, acetone has a flash-point of -20° C. It is entirely possible that 1,1-difluoroethane, which auto-ignited at about 350° C, would have a very low temperature of ignition with a spark or flame.

If it is established that a halogenated hydrocarbon does breakdown somewhere in the range of 100°C to 200°C, that compound (which would then be a FIG) could be used for detection of the early stages of spontaneous combustion, such as in a coal mine pillar in India. Boreholes and sampling tubes, similar to those used by Panigrahi and Bhattacherjee, could be used to see how permeable a coal pillar is, and whether or not spontaneous combustion is developing. A suitable FIG could be introduced, using the sampling tubing, into one of the boreholes on the intake side of the pillar. Boreholes, either surrounding the FIG borehole on the intake side, or on the return side of the pillar, could be monitored for the FIG, and for the breakdown product of the FIG. Potential air permeabilities of a pillar are unknown, and therefore would be the subject of experimentation. Because the air leakage rate is unknown, the amount of FIG needed can not be calculated, but the leakage rate has to be relatively low compared to the airflows in the main return from a large gob. Therefore, a good starting point for the amount of FIG needed in the borehole would likely be somewhere in the range of 10 to 100 grams. Again, only small amounts of samples from surrounding boreholes are needed for analysis. Vacutainers would suffice. Analysis by gas chromatograph/mass spectrograph would provide maximum sensitivity.

Chapter 7: Summary and Conclusions

Coal mine fires that are in inaccessible areas, and therefore are concealed, are a significant problem in all coal mining regions of the world. Some concealed gob fires have lead to explosions that have killed workers. Concealed coal mine fires typically result in months of down-time for the mine, with considerable economic loss. Because they are inaccessible, such fires cannot be easily evaluated, let alone fought. Sometimes, even the existence of a fire in an inaccessible area is difficult to rapidly confirm. The exact location of a fire, and its extent, is sometimes never known; even after the mine has been sealed, and then re-opened. When a mine is sealed, information about whether or not a fire has been extinguished can be difficult to determine. Mines that are sealed to extinguish a fire are occasionally reopened too soon, only to have the fire rekindle. Mines have been sealed for six months, to extinguish a fire; when they might have reopened after four and a half months.

This study details numerous deficiencies with the current practices that are used to try to determine whether or not there is a fire in an inaccessible area of a mine, and makes the point that a more definitive method is needed. This study documents eleven different gas ratios and indices that have been proposed, and used, in order to try to determine whether or not there is a fire in an inaccessible area of a coal mine. With the exception of the hydrocarbon ratio, which has been demonstrated to be late in identifying a fire situation, all the ratios and indices use some combination of the concentrations of O_2, CO_2, and/or CO. All these concentrations are potentially subject to erroneous reading. Any, or all, of them can be diluted, or reduced, by other factors than whether or not there is a fire. Some can be artificially inflated by extraneous factors. There is no way to tell when any reduction or inflation in a gas concentration, unrelated to a fire, is occurring. Gas readings, and ratios and indices derived from them, are not totally reliable, and they typically require long term trending.

Some other method, which does not rely on measuring the concentrations of O_2, CO_2, and/or CO, must be created. This study proposed two such methods:

1. The presence of ^{14}C in CO due to fire.
2. The breakdown of select hydrofluorocarbon compounds in fire to yield novel breakdown products.

The method involving the presence of ^{14}C in CO due to fire was not demonstrated in concept, although there is hope for the future. “Wet” chemistry does not seem to be the way to go. It will be very difficult, if not impossible, to isolate CO, from an atmosphere that contains CO in parts per million, by chemical means. That limitation rules out measuring ^{14}C in CO by liquid scintillation counting, or by accelerator mass spectroscopy. However, the use of laser spectroscopy offers some hope. Special CO_2 laser spectrometers have been custom built at research institutions that can detect ^{14}C in CO_2 at a level of about one part in 10^{15}. ^{14}C is present in the modern CO_2 in the atmosphere at a level of about one part in 10^{12}. That would leave about three orders of magnitude to be taken up by inefficient reaction yield, and dilution of airflows.

However, if CO exiting an inaccessible area increases from a normal, background reading of 2 ppm to an elevated reading of 4 ppm because of a fire, presumably all of the 2 ppm increase is be due to the fire. The 2 ppm increase may be very rich in converted CO_2, with its ^{14}C; and the Boudouard Reaction yield may be reasonably high. In the same line of reasoning, the extra 2 ppm of CO that is seen at the exit of the inaccessible area is after all dilutions of airflows. It does not appear to be impossible, then, that what is now cutting edge instrumentation could become more common, and could be adapted to monitoring the ^{14}C content of CO for coal mine fire detection.

One limitation of the ^{14}C-in-CO method is that it is founded on the Boudouard Reaction, which does not occur at a significant rate below 400°C. This means that the method would not be suitable for detecting the initiation of spontaneous combustion in an inaccessible area, but would be suitable for detecting an incipient fire. If this method became available on a practical basis, one advantage in it is that it is based on a naturally occurring process. This method is not based on introducing a special chemical into an inaccessible area on a batch basis. Monitoring with laser spectrometers could occur on site, on a continual basis.

The second novel method that this study proposed, in order to detect concealed fires, was that of using the breakdown of select fluorinated hydrocarbons compounds. Ideal properties for such fluorinated hydrocarbons were enumerated. A potential source for suitable fluorinated hydrocarbons was identified – the Environmental Protection Agency's list of approved fire extinguishing agents to replace the ozone depleting halons. Although it was realized later, in the experimentation for this study, that the experimental apparatus that was available was not perfectly matched to the experimental needs, the experiments conducted as part of this study nevertheless proved the concept of using fluorinated hydrocarbons as Fire Indicator Gases – with the acronym "FIG." The experimental apparatus could only expose the tested gases to a maximum of 500°C under auto-ignition conditions. An apparatus that would have allowed for the exposure of the gases to a spark, or open flame, would have been better suited to the actual conditions the gases would have been exposed to in a real-world situation.

Five different fluorinated hydrocarbons were tested, and two of the compounds decomposed at 500°C, or less. 1,1-difluoroethane decomposed at 350°C, and C6-perfluoroketone decomposed at 500°C. Both of these compounds decomposed yielding distinctive decomposition products that could be easily identified using a gas chromatograph with a mass spectrograph detector. The breakdown products of 1,1-difluoroethane – fluoroethene and trifluoroethene – are very unlikely to be found in a coal mine under normal operating conditions.

The same holds true for the breakdown product of C6-perfluoroketone – pentafluoroethane.

1,1-difluoroethane is a gas at ambient temperatures. It has a relatively low molecular weight, and a relatively low specific gravity, with respect to that of air. C6-perfluoroketone is a liquid at ambient temperatures, but just barely. It rapidly evaporates. Fire extinguishers, that utilize C6-perfluoroketone, spray it out as a fine mist to rapidly evaporate it. C6-perfluoroketone has a relatively high molecular weight, and a relatively high specific gravity for its vapor, with respect to air.

Both of these FIGs were subjected to decomposition tests that involve combusting the FIG in air, at concentrations of the FIG of 1000 ppm; and then taking a 10 microliter sample of the combustion products and injection this into a gas chromatograph with a 10:1 split ratio. With these protocols, a good signal to noise ratio of 4.1 for 1,1-difluoroethane, and 4.75 for C6-perfluoroketone were obtained. All these facts suggest that the use of these FIGs at initial concentrations of 100 ppm, or somewhat less, is entirely possible; simply by going split-less with the injection into the gas chromatograph, and by increasing the sample size from 10 microliters.

Examples of fire situations were discussed in order to illustrate how FIGs would be used. In particular, FIGs could provide more definitive information to answer the following questions:

1. Is there a fire?
2. Where is the fire located?
3. What is the extent of the fire?
4. Is any effort to fight/contain the fire having any success?
5. When is it safe to reopen the mine?

If mine entries are still accessible to mine personnel, a FIG could be introduced, progressively into different airflows that are entering the inaccessible area, and airflows exiting the inaccessible area could be sampled for the FIG and its breakdown product(s). Introduction could be accomplished by opening a valve to a tank, in the case of a gas like 1,1-difluoroethane, or spraying a mist into the airflow, in the case of a volatile liquid, like C6-perfluoroketone. The amount of FIG that is introduced into the airflow could be based on this study – about 100 ppm to 1000 ppm – unless future work demonstrates that lower concentrations are sufficient. Sampling could be accomplished with gas sample bottles, or with vacutainers. Analysis would be accomplished by gas chromatograph.

If the situation dictates that mine entries are no longer accessible to mine personnel, introduction of a FIG into an inaccessible area could be done with the use of boreholes. A FIG could be put down an available borehole with tubing and a pump, or an induced draft fan. Likewise, recovery of samples could be by tubing and a sample pump, or with a fan.

Analysis by gas chromatograph would be straight forward. The indication of fire is definitive. If breakdown products of a FIG are detected in the airflow that is exiting an inaccessible area, the FIG was exposed to fire temperature. The breakdown products of the two FIGs identified in this study are unusual compounds that will not be routinely present in a coal mine atmosphere. In fact, any fluorinated hydrocarbon, and its breakdown products, would not be routinely present in a coal mine atmosphere. Therefore, false positives should not occur. False negatives could occur, due to dosing an airflow with too small an amount of FIG, associated with too much dilution and diffusion. However, there is a built in safety factor against this kind of false negative, when using FIG technology. A gas chromatograph analysis of a gas sample collected after the FIG has passed through the inaccessible area will allow a determination of the concentration of the FIG after all the dilution and diffusion has occurred. If the concentration of the FIG, after all the dilution and diffusion, is significantly lower than the minimum concentration of the FIG to yield a detectable level of breakdown product, as determined by laboratory tests, then a false negative could be expected. There is another type of false negative. Even if the intake airflow, into an inaccessible area, is dosed to a high enough level with a FIG, only a small fraction of that airflow might be exposed to fire temperatures. Even if the small fraction has a significant amount of FIG breakdown product in it, when the small fraction of airflow is recombined with a much larger total airflow, the concentration of the FIG breakdown product may drop below the limit of detection.

The FIG technology is not based on a naturally occurring reaction, as was the ^{14}C-in-CO method of fire determination. It could not be used for continual monitoring, but would be used on an “as-needed” basis. The FIG method has a potential advantage in that it is adjustable. If it appears that the concentration of FIG is too low, the concentration can be increased. The naturally occurring reaction cannot be adjusted so easily.

Because experiments were conducted with seven different fluorocarbons during this study, an incidental result of this study was the identification of six different fluorinated hydrocarbons that could possibly be used simultaneously as ordinary tracers for the study of complex ventilation problems. A suitable column for their separation was also identified.

Efforts have continued for almost 100 years to develop a definitive test for incipient fires in coal mines. This study makes a detailed argument as to why the old approach of trying to come up with some index, or ratio, of concentrations of O_2, CO_2, and CO cannot result in a definitive test. A different approach is needed. This study suggested, and examined two new approaches. This study introduces the ^{14}C-in-CO concept. Although this concept could not be pursued due to cost constraints, a likely technique is identified – a very sensitive laser spectrometer. Another new approach that this study introduces is that of fire indicator gases – FIGs. A proof of concept is demonstrated for FIGs. This study identifies two fluorinated hydrocarbons that can be used as FIGs, and provides guidance as to how to identify more. In several case studies, details are provided as to how FIGs could be deployed to give definitive answers about coal mine fires. Even if a FIG is not directly exposed to flame in a fire situation, but is exposed to a hot area due to fire, the two FIGs identified in this study would still yield distinctive breakdown products. With a known, inaccessible fire, FIGs can be used to better delineate the location and extent of the fire. These more definitive answers could significantly enhance mine safety, and could result in significant economic savings.

Chapter 8: Recommendations for Future Work

This paper presented two novel methods for definitively determining the presence of fire in inaccessible areas of coal mines: the ^{14}C-in-CO method, and the FIG method.

Although this study was not able to provide a proof-of-concept for the ^{14}C-in-CO method, the method has some advantages that would seem to make the method worth further study. Based on the literature review conducted for this study, the most likely path for future work would seem to be tunable diode laser spectrometers. Such apparatus is already being used to measure the ^{14}C content of CO_2 in the exhaust of passing cars. An adaptation to CO, and an order of magnitude, or two, increase in sensitivity is needed to have this apparatus potentially viable for use with the ^{14}C-in-CO method.

Further study is also needed to better define FIGs. First, FIGs should be studied in the presence of a spark, or open flame. As already noted, auto-ignition is a particularly difficult method for testing chemical compounds for their ability to decompose. For this study, auto-ignition was useful, in that the results of auto-ignition could be representative of the results of a FIG passing through a hot area on the fringes of a fire. However, information on the behavior of FIGs that come in contact with open flames, or sparks, would also be valuable; and would probably be more representative of the situations in which FIGs would be used. Such tests might be done with an adaptation of the equipment used in this study. The reaction tube used in this study had one end sealed with a cap, and the other end closed with a septum in a union fitting. The cap could be removed, and an adaptor put on the fitting for the cap, such that an automobile spark plug could be put on the end of the reaction tube. The spark plug could be fired by the usual automobile electronics. Tests could be done with variable numbers of sparks, and, if necessary, variable temperatures.

Experiments with an open flame might be done initially with something like a propane torch, or a Bunsen burner; with a FIG simply fed continually into the flame. A somewhat more sophisticated method could have the controlled source of flame inside metal ducting that has controlled ventilation due to an adjustable fan. The FIG could be fed into, and mixed with, the airstream at a known rate. Samples for analysis could be gotten at the exhaust end. Such a method could be a good model of a coal mine fire.

More potential FIGs should be tested by decomposing with a flame, including the three proposed FIGs that did not ignite in the auto-ignition tests conducted for this study. As noted above, the three proposed FIGs that did not auto-ignite will decompose at some temperature in the presence of an open flame. 1,1,1,3,3,3-Hexafluoropropane would be particularly interesting to decompose with an open flame, in that it may decompose into an ethane based molecule with a number of fluorine atoms attached. Other compounds that would be interesting to decompose would be 1,1,1-trifluoroethane and 1,1,2-trifluoroethane. Given that an ethane based molecule with two fluorine atoms decomposed relatively easily (1,1-difluoroethane), and an ethane based molecule with four fluorine atoms (1,1,1,2-tetrafluoroethane) apparently decomposes with more difficulty; it would be interesting to see if a trifluoroethane reacts somewhere between the two. Other potential FIGs can be found in any of the complete listings of refrigerants that are available on the internet. Another reason for conducting tests with an open flame is that the decomposition products of the proposed FIGs may vary, from those observed under conditions of auto-ignition.

The reaction of different FIGs, in air, needs to be better defined. The experiments done in this study indicate that, at different temperatures, and with different lengths of time of exposure to high temperatures, different amounts of different breakdown products are observed. This is to be expected. The literature survey on fluorinated hydrocarbons indicated that they did not just decompose straight from the initial compound to the ultimate end products of HF and CO_2. The breakdown reaction for different FIGs with respect to exposure to different temperatures and times does need to be better defined. That will provide information as to what amount of temperature and time will yield the maximum product. Also, it is important to know what amount of temperature and time will result in total destruction of a FIG and all of its breakdown products. Furthermore, a reaction path of sorts can be determined. It is possible that some FIGs will breakdown to an intermediate product that will then breakdown to another product, before finally breaking down into HF and CO_2. C6-perfluoroketone may react that way, yielding 1,1,1,2,3,3,3-heptafluoropropane first; and then pentafluoroethane second. Another possibility is that some FIGs will form more, or different, breakdown products at different conditions of time of exposure, and temperatures. 1,1-difluoroethane may react that way too. 1,1-difluoroethane may breakdown into trifluoroethene and fluoroethene at lower temperatures and/or less time of exposure; but only fluoroethene at higher temperatures and/or more time of exposure. Such details could be valuable in field applications, yielding details about any exposure to fire. Experiments could be conducted with the reaction tube, outfitted with a spark plug. Such experiments could also be conducted with the duct and variable fan that was mentioned above.

Sometimes mines try to fight inaccessible fires by inerting the mine atmosphere with nitrogen. Information on the reaction of FIGs in a nitrogen atmosphere would be useful for these situations. A mine might be able to determine what progress was made in extinguishing fire by using FIGs in a nitrogen atmosphere, if this information was known. The same reaction tube could be used to conduct such experiments.

Only a fraction of the total airflow that would be entering an inaccessible area would be expected to flow through a fire scene. A large enough concentration of a FIG would have to be introduced into the total airflow entering an inaccessible area in order to allow detection of the combustion products at the exhaust end. That detection will be dependant on a diffusion factor, a dilution factor, and a yield factor of the chemical reaction that will yield the products of combustion to be detected. Information on all three factors would be most useful. Work needs to be done to determine the different yield factors for the different FIGs. Again, the basic reactions can be done with the reaction tube fitted with a spark plug. This will also require standards of all the breakdown products, so that the response of the gas chromatograph to each chemical can be determined. Then work needs to be done to determine the different limits of detection for the different reaction products. This determination should be done for a gas chromatograph equipped with an electron capture detector, and for a gas chromatograph equipped with a mass spectrograph detector. The mass spectrograph detector is more sensitive, but the electron capture detector is more readily available. If some FIGs could be used in the field with the electron capture detector, it would mean faster turn-around times for key information during an emergency.

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